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DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

STATEX-93

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY. Volume VI. 1942. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W.I., England. Paper, 9½ by 8¼ inches, 150 pages. Subject and author indexes. Price: I.R.I. members, 2/6; non-members, 10/6.—The important developments in rubber technology and manufacture in a strategic war year are summarized in 22 chapters in the 1942 volume of this series. A short historical and statistical review of that year prefaces authoritative discussions of synthetic rubber, planting and production of raw rubber, chemistry and physics of raw rubber, properties of latex, properties of vulcanized rubber, testing equipment, and compounding ingredients. Wartime conditions in the British Empire are reflected throughout the volume, especially in the chapters on tires, footwear, mechanical rubber goods, insulation, rubber flooring, surgical goods, hose and tubing, hard rubber, and sponge rubber. As in the previous annual reports, both patent and periodical references are numerous and represent current developments in many countries. [From the *India Rubber World: Natural and Synthetic.*]

SYNTHETIC RUBBER: WHAT IT MEANS TO AMERICA. National Synthetic Rubber Corp., Louisville, Kentucky. 8½ x 11½ in. 40 pp.—In an attempt to bring about a broader realization of what the rubber program means to the average American, what synthetic rubbers have already done for industry, and what reasonably may be anticipated for the future, this booklet has been issued jointly by the five companies participating in the ownership and operation of the National Synthetic Rubber Corp., which operates one of the government-owned copolymer plants at Louisville, Kentucky. These companies are: Goodall Rubber Co., Inc., and Hamilton Rubber Mfg. Co., both of Trenton, N. J., Hewitt Rubber Corp., Buffalo, N. Y., Lee Rubber & Tire Co., Conshohocken, Penna., and Minnesota Mining & Mfg. Co., St. Paul, Minn. The booklet describes how the five participating companies worked together to organize the operating company, outlines the management of that company,

includes excellent photographs of various steps in the manufacture of GR-S at Louisville, discusses the importance of synthetic rubber to America, and contians a chart showing the extreme fluctuations of natural rubber prices in the past. Illustrations of the practical uses of synthetic rubbers as developed by the participating companies in the National Synthetic Rubber Corp. are shown in the booklets issued by the various participants. Copies of the booklet can be secured from any one of the participating companies (above) or from the Louisville company. [From *The Rubber Age* of New York.]

THE HISTORY OF RUBBER REGULATION: 1934–1943. Edited by Sir Andrew McFadyean. Published by George Allen & Unwin, Ltd., London, England. Distributed by W. W. Norton & Co., Inc., 70 Fifth Ave., New York, N. Y. 5½ x 8½ in. 240 pp. $3.25.—The International Rubber Regulation Committee was organized as a functioning body in May, 1934, for the purpose of instituting a regulation scheme affecting the principal rubber cultivation areas of the world. It was charged with first effecting a reduction in the abnormally large stocks in existence at that time and thereafter to maintain adequate supplies of rubber at a fair and equitable price. How the Committee was organized, how it functioned, and the results it achieved, are the subject matter of this book, edited by Sir Andrew McFadyean for the Committee. It should be emphasized at this point that the facts are presented in the book; judgment is left to the reader. Although the book is concerned primarily with the functioning of the Committee and a detailed analysis of how decisions concerning cultivation, planting, production, distribution and other factors in the overall rubber picture were arrived at, it includes some general information necessary to round out the full story. Accordingly, the first four chapters of the book are devoted to a general description of rubber and the rubber industry, previous rubber control schemes, negotiations leading up to the formulation of the new Agreement, and principal provisions of the new Regulation and their application, following which are three chapters devoted to the planting of rubber, research and statistics, and stocks of rubber, respectively. These three chapters furnish background information of special importance to the rubber initiate. The remaining five chapters cover the working of the regulation within specific periods. Operations of the Regulation Committee of course carried into the current war period, and from time to time criticism has been leveled at the Committee in connection with the attempt of the United States to amass a huge emergency stockpile of crude rubber prior to December, 1941. One complete chapter in the book is devoted to the history of the constitution of stocks for war purposes, not only in the United States but in the United Kingdom and Canada as well. The factual matter contained in this chapter, covering events of the period in question in considerable detail, should serve to still such criticism for all time. Space does not permit a review of all of the factors involved. The book has twelve chapters in all, and an extensive appendix. This appendix includes the complete text of the International Rubber Regulation Agreement, the names of members of the Committee and of the advisory panel, the text of the cotton and rubber barter agreement (June, 1939), and the complete texts of the first, second, third and fourth agreements entered into between the Rubber Reserve Corporation and the Regulation Committee. The appendix also includes a statistical supplement, containing eleven tables, covering data on total acreage under rubber in regulated areas, new planting and replanting statistics (1934–40), net exports and imports of crude rubber, absorption in importing and producing countries, principal world stocks of rubber (inside and outside of

regulated areas), and average prices for rubber in the London and New York markets from 1910 to 1941. [From *The Rubber Age* of New York.]

RUBBER AFTER THE WAR. By K. E. Knorr. Published by the Food Research Institute, Stanford University, Stanford University, Calif. 6 x 9 in. 46 pp. 25c per copy.—This is the fourth in a series of war-peace pamphlets being published by the Food Research Institute of Stanford University, and is a revision of the series of articles under the same title which ran in the *India Rubber World* from July through October, 1943. Based on a careful study by the author, an acting associate economist at the Food Research Institute, it represents a brief yet detailed analysis of the potentialities of rubber in the postwar period. After giving some background facts and outlining the postwar rubber problem in general, the booklet discusses specific angles, including prospective postwar consumption and supplies, production costs of synthetic rubber, future price competition of natural and synthetic rubber, protection of the synthetic rubber industry, military self-sufficiency, monopolistic control of Malaysian rubber, and the Latin-American situation. In his conclusion, the author states that in the postwar world the United States can obtain a secure rubber supply without resorting to costly protection of a big war-built industry by making provision for a permanent emergency stockpile of crude rubber, regularly amounting to perhaps one year's average consumption and subject to expansion in the event of serious national crisis. [From *The Rubber Age* of New York.]

THE CHEMICAL FRONT. William Haynes. Published by Alfred A. Knopf, Inc., 501 Madison Ave., New York 22, N. Y. 1943. Cloth, 8½ by 5½ inches, 224 pages. Index. Price $3.—Poison gas is a dramatic and terrible aspect of modern warfare on the chemical front, but its significance is minimized by the army of about 1,400 different chemicals which are vital, each in its own way, to victory on the battlefields. William Haynes, former editor of *Chemical Industries*, though revealing no military secrets, summarizes clearly and with unflagging interest the story of the raw materials and processes in the production of superexplosives, high-octane gas, synthetic rubber, smoke-screens, structural light-metal alloys, plastics, and other chemicals of war. The chapter "Chemistry in Politics" reviews the history of the rubber crisis. "Rubber trees flourish no more luxuriantly in the United States than in Germany," Mr. Haynes points out, "but all the heroes of our voluminous detective fiction cannot now find the murderer of rubber preparedness." Seven official bodies originally dealt with the synthetic rubber production problem, but not one of them "ever had authority to approve a plan, provide funds for its execution, and see it through to completion. Waste, confusion, indecision, technical disputes, and political squabbles resulted from this lack of final authority as well as costly changes in plans and priorities. Some examples are cited by the author. Much of what he writes may be true, but in spite of attempts at political interference, the record of the Office of the Rubber Director as given in the six Progress Reports, issued from 1942 to 1944, and actual production irrefutably measured in present synthetic output and its success in keeping "America on wheels" are generally considered in both technical and lay circles outstanding achievements. Mr. Haynes does go on to say that war needs were achieved, and synthetic rubber is here to stay. "Our rubber problem is not going to be solved by the reopening of the Pacific," Mr. Haynes opines, and he holds in the nature of false hopes the millions of dollars spent in recent years to encourage South American rubber production. [From the *India Rubber World: Natural and Synthetic.*]

SYMPOSIUM ON THE APPLICATIONS OF SYNTHETIC RUBBERS. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. 6 x 9 in. 140 pp. $1.50 (paper binding), $1.75 (cloth binding).—The papers and discussions appearing in this volume were presented at Cincinnati, Ohio, on March 2, 1944, during the Spring Meeting of the A.S.T.M. as a special symposium. The aim of the symposium was to present an authoritative compendium of present knowledge on the subject of synthetic rubber, with the full realization that such a summary cannot be complete at this time and might be of somewhat limited permanent value because of the rapid changes taking place. Nevertheless, this small reference volume will prove helpful to the users of synthetic rubber products in aiding them to select intelligently the types of material best suited to their needs and then to use those products under conditions which will assure satisfactory service. The volume includes papers on the origin and development of synthetic rubbers by Fisher (U. S. Industrial Alcohol), physical testing by Cooper (Firestone), physical properties by Ball and Maassen (Vanderbilt), specifications by De France (Goodyear), and an interesting evaluation of processing characteristics and the use of synthetic rubbers in the manufacture of extruded products by Juve (Goodrich). There are also several papers covering specific applications, including tires and tubes by Torrance (du Pont), belting and hose by White (Manhattan Rubber), molded products by Sanger (General Tire), cellular rubber by the late Louis P. Gould, hard rubber products by W. H. Juve, wire and cable by Schatzel (General Cable), footwear by Glover (U. S. Rubber), and adhesives by Wehmer (Minnesota Mining). Every technologist concerned with the production and use of synthetic rubbers and all those who are concerned with this field, even in its non-technical phases, will find this book of definite interest. [From *The Rubber Age* of New York.]

A SUMMARY OF DATA ON SYNTHETIC RUBBER. The Rubber Manufacturers Association, Inc., 444 Madison Ave., New York 22, N. Y. July, 1944. 36 pages.—This digest of information discusses the processes of manufacture and the chemical composition of the five most important synthetic rubbers, other synthetics, and rubber-like materials. Introductory notes give the historical development and statistics and other data on the government program. The booklet was issued primarily as an aid to editors and writers in need of a summary of current facts on this subject. [From the *India Rubber World: National and Synthetic.*]

A SURVEY OF GENERAL AND APPLIED RHEOLOGY. By G. W. Scott Blair. Published by Pitman Publishing Corp., 2 West 45th St., New York 19, N. Y. 5½ x 8½ in. 201 pp. $4.00.—The subject of rheology—the relatively new science of the plastic flow, elasticity and deformation of matter—has not yet, had many books devoted to it, although it is reasonable to assume that the number will grow with the years. The few books which have appeared to date have been devoted largely to theoretical aspects of the subject. The current book is the first to be addressed to the practical rheologist, or, as the author puts it, to "the young physicist, or more often chemist, from whose education, alas, rheology has been almost entirely excluded." The importance of rheology, and its application to the various arts—rubber, plastics, foods, oils, gases, metallurgy, hydro- and aerodynamics, biology—are discussed. Complete, comprehensive treatment of stress-strain-time relations in materials between solids and liquids and the influence of such factors as temperature is given.

Careful consideration is given relationships between rheological properties and chemical constitution. Accurate, tested, usable methods are presented with the minimum of higher mathematics. References to rubber, one of the primary rheological materials, appear throughout the text. The book is divided into two parts, the first devoted to "Rheological Phenomena and Their Measurement" and the second to "Rheological Interpretations and the Evidence of Psycho-Physical Investigations." Each section, in turn, is divided into numerous chapters, covering such subjects as Ideal Materials, Orientation and Surface Phenomena, Rheological Measurements, Theoretical Significance of the Power-Law Relation Between Stress, Strain and Time, Evidence of Psycho-Physics, and General Conclusions. In addition, there is an historical and general introduction, a table of symbols, and a list of abbreviations of technical journals referred to in the text. Complete author and subject indexes are also included. [From *The Rubber Age* of New York.]

THE STORAGE OF 1,3-BUTADIENE (Research Bulletin No. 7.381-C, Second Edition). 8½ x 11 in. 36 pp. THE STORAGE OF ISOBUTYLENE (Research Bulletin No. 7.401-B). 8½ x 11 in. 37 pp. Issued by the Pittsburgh-Des Moines Steel Co., Pittsburgh, Penna.—Four of the most important raw materials in the manufacture of synthetic rubbers are acrylonitrile, 1,3-butadiene, styrene and isobutylene. Because of lack of previous experience in the storage of these raw materials, special research was undertaken to determine best procedures. The data included in these two bulletins, covering 1,3-butadiene and isobutylene, respectively, was compiled under the supervision of James B. Garner, Ludwig Adams and Robert M. Stuchell of the Chemical Storage Research Fellowship maintained at the Mellon Institute of Industrial Research by the Pittsburgh-Des Moines Steel Co., with the collaboration of the engineering department of that company. The bulletins cover the correct physical and chemical properties of the two materials in question as they affect the safe and economic storage of them, as well as the best container materials, suitable protective coatings, proper storage conditions of temperature and pressure, and the most economical type of storage plant, from the standpoint of initial as well as annual operating costs. [From *The Rubber Age* of New York.]

TENSILE STRENGTH TABLE. Kathleen S. Rostler and Hubert I. du Pont Wilmington Chemical Corp., Wilmington, Del. 1944. 28 pages.—This table, prepared for rubber laboratory technicians, offers values for tensile strength in pounds per square inch from the pounds recorded by a testing machine and the thickness of the test-piece, in tensile strength and over the range common in soft rubber compound testing. [From the *India Rubber World: Natural and Synthetic.*]

INFRARED SPECTROSCOPY, INDUSTRIAL APPLICATIONS AND BIBLIOGRAPHY. R. Bowling Barnes, Robert C. Gore, Urner Liddel, and Van Zandt Williams. Published by the Reinhold Publishing Corp., 330 W. 42nd St., New York 17, N. Y. 1944. Fabrikoid, 9¼ by 6 inches, 236 pages. Price $2.25.—Infrared spectroscopy is finding acceptance in industry because it has solved many problems in organic chemistry. This book, important because nearly all organic substances possess selective absorption at certain frequencies in the infrared portion of the electromagnetic spectrum, discusses the theory and its relation to molecular structure. The detailed descriptions of analytic techniques are clues to the progress that has been made in spectrometers and

spectroscopy. More than 350 spectrographs of organic compounds taken in the rock-salt region of the infrared spectrum include aliphatic and aromatic hydrocarbons, alcohols, ethers, carbonyl compounds, nitrogen compounds, terpenes, and organic chlorides. Applications to the synthetic and substitute rubber industries are readily apparent in spectra of butadiene, acrylonitrile, styrene, isoprene, polyvinyl alcohol, ethyl cellulose, and others. The descriptive material and spectrographs have appeared in the November 1943 issue of the *Analytical Edition of Industrial and Engineering Chemistry*. A bibliography of more than 2,700 items has not been previously published. [From the *India Rubber World: Natural and Synthetic*.]

PLASTIC MOLDS. By Gordon B. Thayer. Published by American Industrial Publishers, Fairmount-Cedar Bldg., Cleveland 6, Ohio. 6 x 9 in. 136 pp. $2.50.—This is actually the second edition of a practical guide for designers, builders and users of molds for the handling of plastics. The first edition, issued in 1941, was called "Plastics Mold Designing" (see RUBBER AGE, August, 1941, p. 353). In the new edition, the author has incorporated many suggestions by readers, and has added other material to bring it abreast of new developments in the field. In addition, contributions by five specialists have been included. Several other improvements have been made in the new edition of this book. The Nomenclature of Plastics Molding has been considerably enlarged. In response to a number of requests for a check list to cover the major operations in a contract mold shop, a section on Practical Points in Mold Design and Construction has been added. Specific points to be watched by the toolmaker, the molding operator, the finisher, and the inspector, as well as the designer, are covered in this latter section. This second edition consists of twenty chapters, and includes a subject index. Like the first edition, it should prove of definite value to all designers, manufacturers and users of plastic molds. [From *The Rubber Age* of New York.]

PLASTICS STOCK MOLDS. Compiled and published by Modern Plastics Magazine, 122 East 42nd St., New York 17, N. Y. 8 x 10 in. 182 pp. $5.00. —Illustrations and brief descriptions of nearly 1,600 stock plastic molds, now in the possession of scores of firms throughout the country, as well as nearly 200 standardized extruded cross-sections and standard laminated sheets, rods and tubes, are contained in this catalog. The stock molds, which save countless thousands of man-hours in the manufacture of plastic parts, are classified according to the type of product molded in them. There are 22 classifications in all, from flashlights to smoking accessories. Six separate indices are included to enable the user to locate any type of stock mold and to secure the manufacturer's name and address. Since stock molds have always represented an important segment of plastics production, this catalog should prove of value to every user of molded plastics. [From *The Rubber Age* of New York.]

HACKH'S CHEMICAL DICTIONARY. Third edition. Completely revised and edited by Julius Grant. Published by The Blakiston Co., 1012 Walnut St., Philadelphia 5, Pa. 1944. Cloth, 10 by 6¾ inches, 932 pages. Price $12.— Following the death of Ingo Hackh in 1938, the latest revision of his chemical dictionary was made by Julius Grant, a former collaborator. Concise definitions of more than 57,000 terms used in chemistry, physics, minerology, agriculture, engineering, biology, pharmacy, and medicine are presented. As in previous editions, an effort has been made to achieve a balance between American

and British points of view. The omission of pronunciations is not felt by Mr. Grant to be a serious loss in view of space economies effected. However, though many chemists persist in a personal scheme of pronunciation, a standard authority is desirable. There are 217 tables, diagrams, and portraits. [From the *India Rubber World: Natural and Synthetic.*]

CHEMICAL MACHINERY. An Elementary Treatise on Equipment for the Process Industries. Emil Raymond Riegel. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1944. Cloth, 9¼ by 6 inches, 583 pages. Index. Price $5.—Apparatus and devices which serve a number of diverse chemical processes are given major attention in this volume; highly specialized equipment could not be generously included because of the space limitations necessitated by a single volume of moderate size. Therefore much of the equipment for producing synthetic rubber and its components has been omitted. The content is exact, and useful information and the treatment of the material are descriptive. The text is supplemented with drawings, photographs, charts, and tables. Varying amounts of space and emphasis are allotted to mills and crushers, rubber-lined storage and process tanks, pumps, mixers, conveyer equipment including a traveling rubber tube conveyor, screening and grading equipment, separators, driers, high-pressure equipment, solvent recovery, instruments, and many other devices that have made possible the rapid advance of chemical industries. [From the *India Rubber World: Natural and Synthetic.*]

HANDBOOK OF CHEMISTRY. Fifth Edition. Compiled and edited by Norbert A. Lange. Assisted by Gordon M. Forker. With an Appendix of Mathematical Tables and Formulas by Richard S. Burington. Published by Handbook Publishers, Inc., Sandusky, O. 1944. Fabrikoid, 8 by 5½ inches, 2092 pages. Index. Price $6.—The latest edition, revised and enlarged, of this useful reference volume of chemical and physical data retains the familiar characteristics of earlier editions. All the subject matter has been retained except the table of suffixes (used in the nomenclature of organic compounds) which, together with prefixes and symbols, is now found in a glossary of organic chemistry nomenclature. Six new tables, including one on plastics, have been inserted. Thirteen tables have been extended or completely rewritten, necessitating the addition of 174 pages. The table of physical constants of organic compounds has been increased to 6,507 compounds, with a corresponding list of more than 3,500 synonyms. Many changes have been made throughout the book to insure accurate and up-to-date information. No changes have been made in the synthetic rubber tables. [From the *India Rubber World: Natural and Synthetic.*]

CUMULATIVE INDEX FOR THE CHEMICAL FORMULARY. Compiled by H. Bennett. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. 5½ x 8½ in. 164 pp. $4.00.—This index covers all the formulas included in the first six volumes of THE CHEMICAL FORMULARY, and indicates at a glance the volume and page number for each item in all six volumes. The material has been arranged in strict alphabetical order to facilitate quick reference, with numerous cross-references to enable the user to locate the desired subject, formula or process, as easily as possible. Volumes I to VI of the subject work contain approximately 4,000 pages of tested formulas from every important industry. Each volume is sold at $6.00. [From *The Rubber Age* of New York.]

RUBBER, POLYISOPRENES, AND ALLIED COMPOUNDS

VI. THE MECHANISM OF HALOGEN-SUBSTITUTION REACTIONS, AND THE ADDITIVE HALOGENATION OF RUBBER AND OF DIHYDROMYRCENE.*

GEORGE F. BLOOMFIELD

The chlorination of rubber presents a peculiar feature in that the observed unsaturation of the substitutive chlorination products is considerably lower than would be anticipated for a purely substitutive mode of reaction by the halogen[1]. The possible exercise by the substituent chlorine atoms present in the groups $-CHCl\cdot C:C-$ or $-CH_2\cdot CCl:C-$ of an inhibiting influence on the additive capacity of the double bond can be investigated by examination of halogenated derivatives of rubber and of allied olefins in which the position of the substituent halogen can be established. The work of Ziegler and his collaborators[2] has not only drawn attention to an admirable reagent (*N*-bromosuccinimide) for the halogenation of olefins in the 3-position, but also has provided a method for estimating 3-substituted bromine by interaction with alcoholic silver nitrate.

The action of chlorine on cyclohexene.—The chlorination of cyclohexene appeared to be particularly well suited for examining the details of the chlorination process as it occurs in simple olefins. The behavior of cyclohexene towards chlorine, however, differed from that of the olefins studied previously[1], in that, although the overall chlorination reaction was mainly substitutive (59 per cent, thus giving monochlorocyclohexene, together with trichlorocyclohexane, in which both substitution and addition of chlorine had occurred), yet the major product was the additive dichloride, dichlorocyclohexane. The monochlorocyclohexene had the correct iodine value when allowance was made for the presence of a small proportion of dichlorocyclohexane, from which the chloroölefin could not be completely freed.

Although peroxide-catalyzed chlorination by sulfuryl chloride is normally additive in habit[3], it was found that cyclohexene could none the less be chlorinated in a partly substitutive manner by this reagent if brought to reaction in the presence of an antioxidant or a halogen carrier. The resulting chlorocyclohexene again had the correct iodine value, but whereas all of the chlorine in this chloroölefin could be removed by a brief treatment with alcoholic silver nitrate, only 80–85 per cent of the chlorine was similarly removed from the chlorocyclohexene resulting from the action of chlorine on cyclohexene[4]. Now, since only an insignificant proportion of the chlorine in 1-chlorocyclohexene, and only a relatively small proportion of that in monochlorocyclohexane were removable by comparable treatment with silver nitrate, and, further, since 1-chlorocyclohexene was found to add iodine chloride very incompletely, doubtless owing to the inhibiting effect of the 1-substituted chlorine (cf. dichloroethylene), it must be concluded that the chlorocyclohexene

* Reprinted from the *Journal of the Chemical Society*, April 1944, pages 114–120.

resulting from chlorination by sulfuryl chloride is wholly 3-chlorocyclohexene, whereas that resulting from the chlorination by chlorine is a mixture of this (about 80 per cent), with a smaller proportion (about 20 per cent) of an isomer, likely to be 4-chlorocyclohexene, but containing no 1-chlorocyclohexene. (The 4-chlorocyclohexene is present in slightly greater proportion in the more volatile fractions of the mixture of isomers.)

Unsaturation of halogen-substituted polyisoprenes.—On the assumption that the above considerations apply to the chlorination of dihydromyrcene and of rubber, it must be considered highly improbable that the diminished iodine value observed for mono- and dichloro-substituted dihydromyrcene and for monochloro-substituted rubber can be attributed to an inhibiting effect of the substituent chlorine atom, and hence cyclization must be accepted as the most probable alternative cause. This view finds support in the behavior of the aforementioned substituted derivatives of dihydromyrcene and of rubber towards silver nitrate (see Table).

REACTION OF SOME HALOGENATED SUBSTANCES WITH ALCOHOLIC SILVER NITRATE

Substance	Method of preparation	$100 \times \frac{\text{Reactive halogen}}{\text{Total halogen}}$
Chlorocyclohexene, C_6H_9Cl	Cl+cyclohexene	80—85
Chlorocyclohexene C_6H_9Cl	SO_2Cl_2+cyclohexene+antioxidant	100
1-Chlorocyclohexene, C_6H_9Cl	PCl_5+cyclohexanone	3
Chlorocyclohexane, $C_6H_{11}Cl$		8
Bromocyclohexane, $C_6H_{11}Br$		99
Dichlorocyclohexane, $C_6H_{10}Cl_2$	SO_2Cl_2+cyclohexene+peroxide	1
Chlorodihydromyrcene, $C_{10}H_{17}Cl$	Cl_2+dihydromyrcene	85—90
Bromodihydromyrcene, $C_{10}H_{17}Br$	*N*-Bromosuccinimide+dihydromyrcene	99
Dihydromyrcene dichloride, $C_{10}H_{18}Cl_2$	SO_2Cl_2+dihydromyrcene+peroxide	15
Chlororubber, $C_{10}H_{15}Cl$	Cl+rubber	88
Chlororubber, C_5H_7Cl	Cl+rubber	70
Chlororubber, $C_{10}H_{15}Cl$	SO_2Cl_2+rubber+antioxidant	90
Bromorubber, $C_{10}H_{15}Br$	*N*-Bromosuccinimide+rubber	94
Rubber dichloride, $C_5H_8Cl_2$	SO_2Cl_2+rubber+peroxide	6

If the small proportion of the chlorine in these derivatives which is unreactive to silver nitrate is attributed to 1-substituted products, then the amount of these is quite insufficient to account for the whole of the observed lowering of iodine value; indeed, it seems more justifiable, as in the case of cyclohexene, to attribute the unreactive part of the chlorine to substitution in positions other than the methinic and α-methylenic carbon atoms, *i.e.*, to substitution in the β- or β'-positions, and such substitution would cause no lowering of the iodine value. Furthermore, monobromodihydromyrcene obtained by the action of *N*-bromosuccinimide on dihydromyrcene has almost the theoretical iodine value (cf. the low iodine value of monochlorodihydromyrcene obtained by the action of chlorine on dihydromyrcene), and all of its halogen is removed by silver nitrate[5]. The behavior of the bromorubber similarly obtained is not, however, so satisfactory, its iodine value being considerably lower than that required for simple bromine substitution. Since there is no justification for assuming that the mode of reaction of *N*-bromosuccinimide should be any different in the case of rubber from that established with the considerable number of olefins which have been successfully brominated at the α-methylenic position, this reduction of unsaturation is again attributed to cyclization.

The further chlorination of monochloro-substituted rubber provides evidence in support of a cyclized structure. Reference has already been made[1] to the additive uptake of only 0.5 mole of chlorine per C_5H_7Cl unit, which is in accordance with the observed unsaturation. It is now found that an excess of sulfuryl chloride reacting under additive conditions in the presence of a peroxidic catalyst also brings about the addition of only 0.5 mole of halogen, the

rest reacting substitutively. It is, therefore, concluded that the chlorination of polyisoprenes is particularly prone to proceed by a cyclization mechanism. The cyclization appears to be complete with rubber (leaving $|_1^-$ per two C_5H_7Cl units) but only partial with dihydromyrcene (about 30 per cent of molecules cyclized); no separation of cyclized and uncyclized portions is practicable, owing to the proximity of boiling points.

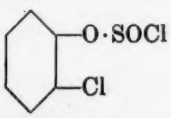
Formation of polychloro derivatives in chlorination reactions.—Although the ratio of liberated hydrogen chloride to reacted chlorine permits of the formation of only a monosubstituted chloro derivative from rubber, the possibility of tri- or polychloride formation, as well as additive chlorination, must be taken into account when this ratio falls below unity. In the case of cyclohexene the formation of a considerable proportion of trichlorocyclohexane has been established, the relative proportions of the chlorination products from this olefin being dichlorocyclohexane 47 per cent, trichlorocyclohexane 23 per cent, 3-chlorocyclohexene 19 per cent, 4-chlorocyclohexene 5 per cent, residue (containing much chlorine) 6 per cent. 1-Methylcyclohexene appears to yield mainly monochloromethylcyclohexene and trichloromethylcyclohexane, with relatively little dichloromethylcyclohexane. Where these polychloro derivatives are formed the yield of monochloroölefin is considerably less than would be expected from the proportion of hydrogen chloride formed, *e.g.*, the simultaneous progress of reactions (1) and (2):

$$RH|_1^- + Cl_2 \rightarrow RCl|_1^- + HCl \qquad (1)$$

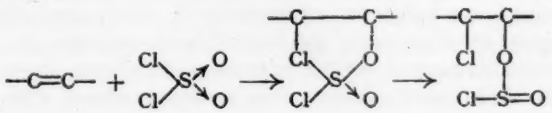
$$RH|_1^- + 2Cl_2 \rightarrow RCl_3 + HCl \qquad (2)$$

satisfies an overall reaction which is apparently 67 per cent substitutive as measured by the hydrogen chloride: chlorine ratio, but the yield of monochloro-substitution product is only 33 per cent when calculated on the amount of chlorine reacting.

Polychloride formation is greatest with cyclohexene, even when the hydrocarbon is present in considerable excess; doubtless, the increase in monosubstitutive reaction in 1-methylcyclohexene, dihydromyrcene, squalene, and rubber is to be attributed to the influence of the 1-methyl substituent. No chloro derivatives other than monochloroölefin and additive dichloride are, however, obtained when sulfuryl chloride is used as a substitutive chlorinating agent, although, in the absence of a halogen carrier, a small amount of the chloride of 2-chlorocyclohexyl sulfite (inset) is formed[30].

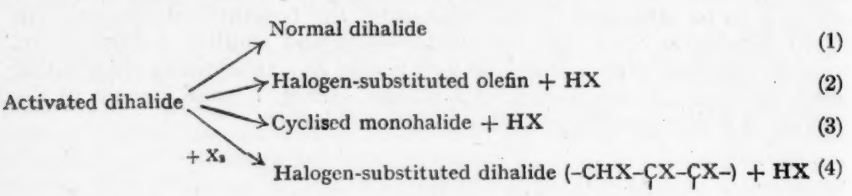


This substance is assumed to have resulted by addition of sulfuryl chloride to the ethylenic linkage, since Kharasch and his collaborators[6] have shown that substitution of $-SO_2Cl$ groups by a free-radical chain mechanism leads to the formation of sulfonyl chlorides. Since the sulfur atom is linked to the carbon atom through oxygen, the additive reaction is thought to pursue the molecular course:



The intermediate formation of the chloride of 2-chlorocyclohexyl sulfite has been assumed by Friese and Djiang[7] to occur in the reaction of sulfuryl chloride with cyclohexene and acetic acid, whereby 1-chloro-2-acetoxycyclohexene is isolated as a final product.

The reaction of chlorine with rubber and with allied olefins, which does not appear to follow a free-radical course, since it proceeds with equal facility in darkness and in light and in the presence or absence of oxygen, antioxidants, or peroxides, very probably depends on the activating effect of the $-CMe:C-$ system on the left-hand α-methylene hydrogen atoms of $-CH_2 \cdot CMe:CH \cdot CH_2-$[8] leading to preferential substitution at this position, and this view is supported by the decrease in additive reaction in passing from cyclohexene to 1-methylcyclohexene, dihydromyrcene, squalene, and rubber, although the mode of reaction with rubber may be influenced by the readiness with which this undergoes cyclization. It is, however, necessary to consider whether the reaction of molecular chlorine is truely substitutive or whether it involves double bond reformation or cyclization changes, either spontaneous or promoted by an intermediate additive chloride of high energy content. The very considerable stability of the additive chlorides of cyclohexene, dihydromyrcene, and rubber (see below) renders extremely doubtful any hypothesis of secondary decomposition of an additive dichloride. The possibility of an induced decomposition of an additive dichloride[9] has been examined by submitting an additive dichloride of rubber to the action of chlorine; although some substitutive reaction occurred whereby the chlorine content was raised, there was no evidence of any significant elimination of hydrogen chloride other than that accounted for by the substitutively-reacting chlorine, nor was there evidence of any double bond reformation. There still remains the possibility that reaction proceeds by a chain mechanism involving a resonance hybrid[10], or alternatively by formation of an activated additive dihalide of high energy content[29], deactivation of the latter proceeding in one or more of the following ways according to the prevailing reaction conditions, the energy associated with the activated dihalide, and the nature of the olefinic system:



Whether the halogenation reactions now under consideration are actually substitutive, or whether they proceed in accordance with the above hypotheses, cannot be finally established from the evidence available, but the bulk of the evidence rather favors a mechanism conforming with Stewart's proposals. The cyclization mechanism (3) seems somewhat preferable to that suggested[11], since in the new scheme it is no longer necessary to assume a different point of attack of the halogen in the polyisoprene and cyclohexene systems.

The additive halogenation of rubber and of dihydromyrcene.—It seemed desirable to examine some halogenation reactions in which the halogen is generated by decomposition of an easily dissociated halogeno reagent. Phenyliodochloride is a suitable reagent for this purpose and has been shown by Garvey, Halley, and Allen[12] to form additive chlorination products with cyclohexene

and other olefins. These workers have also shown that phenyliododifluoride reacts with rubber to give hydrogen fluoride and a monofluororubber, the latter being formed either substitutively or by decomposition of an unstable difluoride. It was accordingly anticipated that phenyliododichloride would yield a monochlororubber and hydrogen chloride in the same way as chlorine itself, and indeed, Garvey, Halley and Allen[12] have stated generally that the mode of chlorination by this reagent is the same as that of chlorine. Surprisingly, this reagent has been found to halogenate rubber in an almost exclusively additive way, yielding a dichloride $(C_5H_8Cl_2)_n$ of considerable thermal stability compared to products of substitutive chlorination.

The chlorinating action of peroxide-catalyzed sulfuryl chloride[13] has already been used for the addition of chlorine at the ethylenic linkage of cyclohexene[3], and this reagent has now enabled chlorine addition products to be obtained from dihydromyrcene and from rubber, although some difficulty was experienced in obtaining wholly additive reaction with specimens of rubber which had not been submitted to careful purification to remove naturally occurring antioxidants.

The formation of a stable additive dichloride of rubber is of considerable theoretical interest, since a purely additive reaction free from substitution has not hitherto been achieved. An additive dibromide, $(C_5H_8Br_2)_n$, on the other hand, was prepared long ago[14], and indeed, attempts have been made to estimate rubber hydrocarbon by bromine addition, although the formation of the dibromide has not generally been accomplished without the liberation of some proportion of hydrogen bromide, and the dibromide when isolated has been reported to liberate hydrogen bromide vigorously at 50–60°[15]. Substitutive side reaction has, however, been minimized by operating at 0° in chloroform[16].

A more detailed study of the manner of reaction of bromine with rubber appeared desirable, since it seemed to occupy an interesting intermediate position between the exclusively substitutive mode of reaction of chlorine and the exclusively additive mode of reaction of iodine chloride[17]. When rubber was acted upon by bromine at temperatures between 0° and −40°, no difficulty was experienced in obtaining an exclusively additive reaction, provided that some chloroform was present, and the bromide so obtained underwent no decomposition at all on heating to 80°, nor was there any evidence of change in unsaturation, such as might arise from double bond reformation or from cyclization, as a result of mild heat treatment of a partly brominated product. The effect of chloroform in suppressing a substitutive reaction is probably due to traces of alcohol normally present in this solvent rather than to any special characteristic of the solvent itself, since addition of alcohol enabled bromination to be conducted in carbon tetrachloride without hydrogen bromide formation: in this connection it is of interest that an alcoholic medium has been found helpful in suppressing substitutive reaction in the preparation of dihydromyrcene tetrabromide.[18]

In spite of statements to the contrary in the literature, bromine addition has in the present work been found satisfactory for estimating rubber hydrocarbon, and it has the special merit of speedy operation.

Mechanism of additive halogenation reactions.—Kharasch and Brown[19] suggest that the twofold mode of reaction of sulfuryl chloride can be explained by the following hypotheses: (1) The peroxide-catalyzed reaction furnishes a source of chlorine atoms, and chlorination proceeds by a free-radical chain mechanism. (2) Thermal dissociation of the reagent provides some other form of active chlorine, which reacts in the same way as chlorine itself. In the

former case, the reaction mechanism is of the same nature as that proposed for photochemical chlorination[20], which even in a simple substitutive reaction may follow a course quite different from that promoted by chlorine in the absence of direct illumination, for, whereas photochemical chlorination with chlorine[21] and the peroxide-catalyzed reaction of sulfuryl chloride both lead to substitution of fatty acids in the β-position (mainly), yet nonphotochemical chlorination carried out with chlorine[22] or with sulfuryl chloride in the presence of a halogen carrier yields α-substituted acids.

If these hypotheses are accepted in the present investigation, then, if it can be shown that chlorination by phenyliodochloride follows a free-radical course, there will be reason to think that the presentation of the chlorine in free radical, *i.e.*, atomic, form is also an essential condition for the additive chlorination of rubber and of allied olefins. Although the reaction with phenyliodochloride gave in practice no obvious sign of being peroxide-catalyzed, there was evidence of an underlying free-radical chain mechanism in the fact that the reaction in the presence of quinol was very slow and incomplete, and was also to a considerable extent substitutive in character. Zappi and Degiorgi[23] have differentiated between the electrical charges associated with the two chlorine atoms in phenyliodochloride; hence the separation of a free chlorine atom by thermal dissociation (Equation 1) is not an unlikely initiating step, although in the presence of a peroxide the steps shown in Equations 2–4 represent a more probable course of reaction. After the liberation of atomic chlorine,

$$PhICl_2 \rightarrow PhICl^{\cdot} + Cl^{\cdot} \quad (1)$$

$$Peroxide \rightarrow R^{\cdot} \quad (2)$$

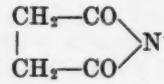
$$R^{\cdot} + PhICl_2 \rightarrow RCl + PhICl^{\cdot} \quad (3)$$

$$PhICl^{\cdot} \rightarrow PhI + Cl^{\cdot} \quad (4)$$

the reaction could quite well proceed by the chain mechanism proposed for sulfuryl chloride[19].

Attempts have been made to confirm the requirement of atomic chlorine for obtaining the additive chlorination of rubber by bringing chlorine into contact with a rubber solution which was irradiated by a powerful ultraviolet lamp, and also with a rubber solution containing benzoyl peroxide (the latter experiment being conducted at 80°), but in neither case was there any obvious departure from the usual exclusively substitutive reaction of the chlorine. Probably the substitutive reaction of molecular chlorine proceeds more readily than the additive reaction of free radical chlorine when both forms of the reagent are present.

An explanation of the substitutive bromination of olefins by *N*-bromosuccinimide presents rather more difficulty, but a chain mechanism of the type represented by Equations 5–8 provides a satisfactory explanation if it be assumed that the major influence directing the reaction is the tendency of the



radical (formed in the first instance by thermal dissociation of the bromocompound) to accept hydrogen (6) and that the α-methylene hydrogen atom is the one most readily detached from the $-CH_2 \cdot CR{:}CH-$ system.

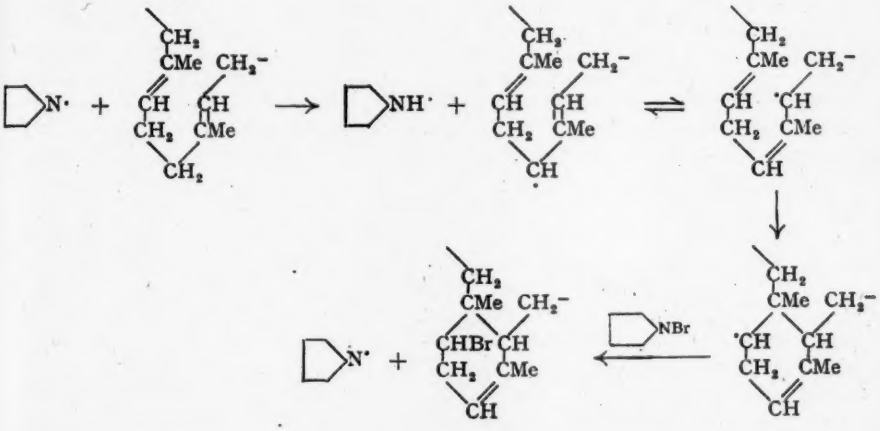
$$(C_4H_4O_2)N\cdot Br \rightarrow (C_4H_4O_2)N^{\cdot} + Br^{\cdot} \quad (5)$$

$$-CH_2\cdot C{:}C- + (C_4H_4O_2)N^{\cdot} \rightarrow -\dot{C}H\cdot C{:}C- + (C_4H_4O_2)NH \quad (6)$$

$$-\dot{C}H\cdot C{:}C- + Br^{\cdot} \rightarrow -CHBr\cdot C{:}C- \text{ (or } -C{:}C\cdot CHBr-) \quad (7)$$
(chain termination)

$$-\dot{C}H\cdot C{:}C- + (C_4H_4O_2)N\cdot Br \rightarrow \underset{(\text{or } -C{:}-\cdot CHBr-)}{-CHBr\cdot C{:}C-} + (C_4H_4O_2)N^{\cdot} \quad (8)$$
(chain propagation)

The production of isomeric bromo-substituted products in reactions (7) and (8)[2] is to be anticipated as a result of resonance in the $-\dot{C}H\cdot C{:}C-$ radical[24], and the very considerable degree of cyclization promoted by the action of *N*-bromosuccinimide on rubber can be similarly explained by the following mechanism.



EXPERIMENTAL[25]

In general, the chlorination apparatus already described[26] was used. For halogenating agents other than chlorine, the graduated tube *A* was removed; liquid reagents were introduced beneath the surface of the rubber solution in *B*, and for this purpose a dropping funnel was fitted. A stirrer was also introduced into *B* to ensure thorough mixing of liquid and solid reagents. Gaseous reaction products were swept into an absorption system by means of a brisk stream of purified nitrogen which also prevented access of air to the reaction system.

Treatment of halogenated products with alcoholic silver nitrate.—The sample (0.1 g.) was dissolved in a little alcohol, alcoholic silver nitrate (25 cc., 0.1 *N*) added, and the solution heated under reflux for 30 min. After cooling, the solution was suitably diluted and an aliquot portion was added to an excess of sodium chloride solution (0.025 *N*), the excess being estimated volumetrically with silver nitrate solution (0.025 *N*), dichlorofluorescein being used as internal indicator.

Alcohol-insoluble substances, *e.g.*, halogenated rubbers, were dissolved in benzene (0.1 g. in 100 cc.), and to the solution, warmed to 50–60°, was added a mixture (50 cc.) of equal volumes of alcoholic silver nitrate (0.1 *N*) and ben-

zene. After refluxing for 1 hour and subsequently cooling, the solution was washed with successive small quantities of water until free from silver; the washings were combined, and an aliquot portion treated as above.

The proportion of the halogen which reacted with the silver nitrate, expressed as a percentage of the halogen in the sample, is hereinafter described as *reactive halogen*.

HALOGENATION WITH CHLORINE

The action of chlorine on cyclohexene.—Peroxide-free cyclohexene (20 cc.; prepared by shaking with aqueous sodium hyposulfite, drying in an inert atmosphere, and distilling in a stream of purified nitrogen) was treated with chlorine (14.4 g.) at 80° in the absence of oxygen and in very subdued light: 4.33 g. of hydrogen chloride was formed, corresponding to 59% substitutive reaction. Distillation of the liquid product (26.2 g.) gave the following fractions: (1) unreacted cyclohexene; (2) b. p. <40°/13 mm. (1.0 g.); (3) b. p. 40–50°/13 mm. (2.0 g.); (4) b. p. 50–60°/13 mm. (2.5 g.); (5) b. p. 60–68°/13 mm. (found: I value 31) (2.4 g.); (6) b. p. 68–70°/13 mm (found: I value 9) (1.6 g.); (7) b. p. 70–72°/13 mm. (2.1 g.); (8) b. p. 30–52°/0.01 mm. (2.1 g.); (9) b. p. 52–53°/0.01 mm. (2.8 g.); (10) b. p. 53–60°/0.01 mm. (0.4 g.); (11) small residue (1.0 g.). Fractions (8)–(10) were saturated to iodine chloride and to bromine, (6) and (7) were mainly 1:2-dichlorocyclohexane (cf. product of reaction of sulfuryl chloride with cyclohexene), and (9) was a trichlorocyclohexane (found: Cl, 56.7; calcd. for $C_6H_9Cl_3$: Cl, 56.8%). The bulk of the unsaturated products were in the more volatile fractions; (3) and (4) were accordingly united and redistilled, yielding fractions (12) b. p. 38–40°/13 mm. (1.2 g.); (13) b. p. 40–43°/13 mm. (1.5 g.); (14) b. p. 43–65°/13 mm. (0.6 g.); and (15) b. p. 65–68°/13 mm. (1.2 g.). The last fraction was saturated to iodine chloride and was added to the dichlorocyclohexane fractions. The foregoing separative procedure thus yielded the following main products: monochlorocyclohexene (4.3 g.), dichlorocyclohexane (8.4 g.), and trichlorocyclohexane (4.2 g.). Fractions (12) and (13) comprised the chlorocyclohexene but were not entirely free from dichloro derivatives [found for (12): C 61.1; H 7.75; Cl 31.1; reactive Cl 23.1; I value 205. Calcd. for a mixture of 95.5% C_6H_9Cl and 4.5% $C_6H_{10}Cl_2$: C 61.1; H 7.7; Cl 31.2%; I value 208; found for (13): C 60.4; H 7.7; Cl 31.6; reactive Cl 23.5; I value 204. Calcd. for a mixture of 91.8% C_6H_9Cl and 8.2% $C_6H_{10}Cl_2$: C 60.65; H 7.7; Cl 31.75%; I value 200].

1-Chlorocyclohexene was prepared by the action of phosphorus pentachloride on cyclohexanol-free cyclohexanone[27], and was freed from unreacted cyclohexanone by treatment with semicarbazide hydrochloride; the purified liquid had b. p. 35°/13 mm. (found: C 61.6; H 7.8; Cl 30.55; reactive Cl <1; I value 125. Clacd. for C_6H_9Cl: C 61.8; H 7.8; Cl 30.4%; I value 218).

Monochlorodihydromyrcene was prepared by the action of chlorine on a considerable excess of dihydromyrcene[1], but it was difficult to separate the chlorination product from the excess hydrocarbon. The following fractions were examined: (1) b. p. 33–38°/13 mm. (found: Cl 8.25; reactive Cl 7.5; I value 315. Calcd. for mixture of 40% $C_{10}H_{17}Cl$ and 60% $C_{10}H_{18}$: Cl 8.25%; I value 329); (2) b. p. 38–43°/13 mm. (found: Cl 13.3; reactive Cl 11.8; I value 298. Calcd. for mixture of 64.5% $C_{10}H_{17}Cl$ and 35.5% $C_{10}H_{18}$: Cl 13.3%; I value 320); (3) b. p. 43–46°/13 mm. (found: C 70.6; H 10.0; Cl 19.25; reactive Cl 18.6; I value 278. Calcd. for mixture of 93.5% $C_{10}H_{17}Cl$ and 6.5% $C_{10}H_{18}$: C 70.7; H 10.1; Cl 19.3%; I value 299).

Two monochlororubbers were prepared as described before[1] [found: (1), Cl 35.95 (34.6% substituted); reactive Cl 24.4%. (2), Cl 17.75 (all substituted); reactive Cl 15.5%; I value 224].

Halogenation with phenyliododichloride.—To purified rubber hydrocarbon[23] (5 g.) dissolved in carbon tetrachloride (300 cc.) was added phenyliododichloride (19.2 g., 0.95 mole per C_5H_8 unit), and the suspension was heated to boiling with stirring; a brisk reaction set in, and a colorless homogeneous solution resulted. A little hydrogen chloride (0.1 g., corresponding to <4% substitutive reaction) was evolved. The product, polyisoprene dichloride, isolated by precipitation with alcohol, was a white, fibrous mass (10 g.), readily soluble in most rubber solvents (found: C 45.4; H 6.0; Cl 48.1; I value 16; intrinsic viscosity $[\eta]$ in benzene, 2.125, indicating probable M, 127,000. Calcd. for 96% additive reaction of 0.95 mole reagent: C 44.65; H 5.9; Cl 49.45%; I value 17). Additive reaction to the extent of 98% was observed when acetone-extracted crepe rubber was brought to reaction in a similar manner but with benzoyl peroxide (4% of weight of rubber) present; when, however, quinol was substituted for the peroxide only 86% of the reagent was utilized in 30 min. at the b. p., and 27% of the reacted phenyliododichloride chlorinated the rubber substitutively.

Action of chlorine on polyisoprene dichloride.—Chlorine (2.1 g.) was passed slowly in bright light through a carbon tetrachloride solution (300 cc.) of the dichloride (4 g.). The halogen did not react very readily, and only 0.7 g. was consumed; a little hydrogen chloride (0.3 g.) was formed. The product was a white, fibrous substance (found: Cl 53.05; I value 0; $[\eta]$ in benzene, 1.58, indicating probable M, 94,000. Calcd. for substitutive reaction of 0.6 g. and additive reaction of 0.1 g. chlorine: Cl 53.0%).

HALOGENATIONS WITH SULFURYL CHLORIDE

Method.—The reagent was diluted with an equal volume of carbon tetrachloride and run into the solution of the olefin in carbon tetrachloride at the b. p. of the latter, in the dark, and in an atmosphere of nitrogen. For the absorption system two wash-bottles containing water and a third containing aqueous sodium hydroxide (5%) were used; in the first two bottles the bulk of the sulfur dioxide and all of the hydrogen chloride formed were absorbed, and any sulfuryl chloride carried over with the gaseous reaction products was hydrolyzed to hydrochloric and sulfuric acids. The third bottle trapped any sulfur dioxide swept out of the aqueous solution. The sulfur dioxide was determined iodometrically, the sulfuric acid gravimetrically, and the hydrochloric acid volumetrically (dichlorofluorescein indicator) after oxidation of sulfur dioxide with hydrogen peroxide. From the amount of hydrogen chloride formed was deducted a quantity equivalent to the sulfuric acid found to allow for sulfuryl chloride hydrolyzed, in accordance with the equation $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$, and from the remaining hydrogen chloride was calculated the extent of substitutive chlorination, in accordance with the equation $RH + SO_2Cl_2 = RCl + HCl + SO_2$.

Chlorination of cyclohexene in presence of peroxide.—In Kharasch and Brown's preparation[19] of dichlorocyclohexane, b. p. 66–68°/13 mm. (found: C 47.2; H 6.7; Cl 46.1; reactive Cl 0.4. Calcd. for $C_6H_{10}Cl_2$: C 47.05; H 6.6; Cl 46.35%), the sulfur dioxide formed corresponded to utilization of 90% of the reagent, and the hydrogen chloride formed corresponded to <5% substitutive reaction.

Chlorination of cyclohexene in presence of antioxidant.—Sulfuryl chloride (22.5 g.), reacting with peroxide-free cyclohexene (50 g.) in the presence of quinol (0.2 g), yielded after removal of excess cyclohexene a liquid product (22.5 g.), together with sulfur dioxide (8.3 g., 78% utilization of reagent in substitutive and additive reactions) and hydrogen chloride (0.82 g.) corresponding to 14% substitutive reaction; 5.5% of the reagent was swept out of the reaction flask. Distillation of the liquid product gave the following fractions: (1) b. p. 55–65°/13 mm. (5.9 g.); (2) b. p. 65–70°/13 mm. (9.2 g.); (3) b. p. <74°/0.002 mm. (2.4 g.); (4) b. p. 74°/0.002 mm. (3.6 g.); (5) residue (0.5 g.). Redistillation of fraction (1) gave sub-fractions (6) b. p. 40–65°/13 mm. (3.4 g.), containing unsaturated material, and (7) b. p. 65–68°/13 mm. (2.3 g.), saturated to iodine chloride. Fractions (2) and (7), total 11.7 g., were mainly dichlorocyclohexane (found: C 47.95; H 6.7; Cl 45.2%). Redistillation of fractions (3) and (4) gave the *chloride* of *2-chlorocyclohexyl sulfite*, v. p. 74°/0.002 mm.; some sulfur dioxide was liberated before its analysis could be carried out [found: C 34.2; H 4.75; Cl 33.65; S 13.6. $C_6H_{10}Cl_2(SO_2)_{0.9}$ requires C 34.2; H 4.8; Cl 33.65; S 13.7%]. An identical liquid resulted from the action of thionyl chloride on cyclohexanol at 0°[30]. The chloride reacted with water with evolution of heat, liberating 1 mole of hydrogen chloride and less than 1 mole of sulfur dioxide, so yielding a liquid product which gave on distillation mainly 2-chlorocyclohexanol (found: C 53.3; H 8.3; Cl 26.4; OH, 12.7. Calcd. for $C_6H_{11}OCl$: C 53.55; H 8.25; Cl 26.35; OH 12.6%) and a nonvolatile solid residue, believed to be *bis-(2-chlorocyclohexyl) sulfite*, m. p. 92° from light petroleum (found: C 45.95; H 6.5; Cl 22.65; S 10.2. $C_{12}H_{20}O_3Cl_2S$ requires C 45.7; H 6.4; Cl 22.5; S 10.15%).

Chlorination of cyclohexene in presence of iodine.—Sulfuryl chloride (16.7 g.), cyclohexene (30 g.), and iodine (0.2 g.) required 1½ hours at 80° for completion of reaction, and yielded a liquid product (15.5 g.) with sulfur dioxide (6.4 g., 81% utilization of reagent) and hydrogen chloride (1.28 g., 35% substitutive reaction of reagent utilized). The liquid gave the following fractions: (1) b. p. 30–60°/13 mm. (3.6 g.), (2) b. p. 60–68°/13 mm. (10.2 g.): the latter fraction was mainly dichlorocyclohexane. Fraction (1) was united with fraction (6) of the preceding experiment; redistillation gave a main fraction, b. p. 52–55°/13 mm. (5.0 g.), which was principally 3-chlorocyclohexene (found: C 59.2; H 7.6; Cl 32.9; reactive Cl 25.7; I value 182. Calcd. for a mixture of 82.6% C_6H_9Cl and 17.4% $C_6H_{10}Cl_2$: C 59.2; H 7.6; Cl 33.2%; I value 180).

Peroxide-catalyzed chlorination of a chloro-substituted rubber $(C_5H_7Cl)_n$.—A solution in carbon tetrachloride of a chlororubber [(*a*), see above (Cl, 35.95%)], obtained by the action of chlorine on rubber (4.0 g.), was treated with sulfuryl chloride (9.0 g., 1.25 moles per C_5H_8 unit) and benzoyl peroxide (0.2 g.) at 80° in a nitrogen atmosphere in the dark. Reaction was incomplete in 2 hours, and there were formed in this time sulfur dioxide (3.75 g.), corresponding to 7.7 g. of reacted sulfuryl chloride (*i.e.*, 1.02 moles. per C_5H_8 unit), and hydrogen chloride (1.11 g.), corresponding to additive reaction of 3.75 g. of reagent (0.49 mole per C_5H_8 unit) and substitutive reaction of 4.15 g. of reagent.

Peroxide-catalyzed chlorination of dihydromyrcene.—Sulfuryl chloride (16.7 g.) and dihydromyrcene (44 cc., 1 mole reagent per $|_4^=$) reacting in the presence of benzoyl peroxide (0.2 g.) yielded a liquid product (38 g.) together with sulfur dioxide (7.25 g.) and hydrogen chloride (0.2 g.). The liquid gave the following fractions on distillation: (1) dihydromyrcene, b. p. 55–58°/13 mm. (14.9 g.); (2) b. p. <55°/0.2 mm., mainly dihydromyrcene (2.5 g.); (3) b. p. 55–56°/0.2

mm. (14.5 g); (4) b. p. 56–60°/0.2 mm. (1.7 g.); (5) b. p. <74°/0.002 mm. (1.9 g.); (6) 74–78°/0.002 mm. (2.5 g.); residue (1.2 g.). Fraction (3) was *dihydromyrcene dichloride* (found: C, 57.65; H 8.6; Cl 33.45; reactive Cl 5; I value 128. $C_{10}H_{18}Cl_2$ requires C 57.4; H 8.7; Cl 33.9%; I value 122). Fraction (6) had I value 74, and was probably mainly dihydromyrcene tratrachloride (see below).

Sulfuryl chloride (26.2 g.; 2 moles) reacted with dihydromyrcene (13.4 g.; 1 mole) in the presence of benzoyl peroxide (0.2 g.) to give a liquid product (27 g.), with sulfur dioxide (11.35 g.) and hydrogen chloride (0.34 g.). Distillation of the liquid yielded *dihydromyrcene tetrachloride* (18.6 g.), b. p. 82–90°/0.002 mm. (found: C 43.35; H 6.5; Cl 50.0; I value <2. $C_{10}H_{18}Cl_4$ requires C 42.9; H 6.5; Cl 50.6%), together with a little liquid (0.8 g.) of lower b. p. and some residue (3.8 g.). Part of the dihydromyrcene tetrachloride crystallized on standing; the crystals (from methanol) had m. p. 50° (found: C 42.9; H 6.55; Cl 50.7%).

Peroxide-catalyzed chlorination of rubber.—The rubber (4 g.)[28] was dissolved in carbon tetrachloride (250 cc.) under conditions precluding access of air, and allowed to react at 80° with sulfuryl chloride (7.8 g.) in the presence of benzoyl peroxide (0.1 g.); there were formed sulfur dioxide (3.5 g.) and hydrogen chloride (0.1 g.). The reaction product (8.0 g.), isolated by precipitation with alcohol, was indistinguishable from the *polyisoprene dichloride* described above (found: C 43.1; H 5.7; Cl 51.25; reactive Cl 3; I value 14; $[\eta]$ in benzene, 2.015, indicating probable M, 120,000. $C_5H_8Cl_2$ requires C 43.1; H 5.75; Cl 51.15%; I value 0). This product was stable in air and at 80°.

From crepe rubber (10 g.) and sulfuryl chloride (10 g.), there were formed sulfur dioxide (4.4 g.), hydrogen chloride (2.2 g.), and a rubberlike product (12 g.), which was unstable on exposure to air or on heating (found: Cl 23.0; reactive Cl 16.5. Calcd. for 90% substitutive and 10% additive reaction: substituted Cl 18.5; total Cl 23.5%). From acetone-extracted crepe rubber (5 g.) and sulfuryl chloride (5 g.) there was similarly obtained 0.6 g. of hydrogen chloride, corresponding to 45% substitutive reaction.

HALOGENATION WITH *N*-BROMOSUCCINIMIDE

Bromination of dihydromyrcene.—*N*-Bromosuccinimide (18 g., 1 atom Br per $C_{10}H_{18}$) and dihydromyrcene (17.7 cc.) in carbon tetrachloride (100 cc.) were kept at 77° in an atmosphere of nitrogen; no hydrogen bromide was liberated. Distillation of the product, after separation of succinimide (9.9 g.), yielded a liquid fraction, b. p. 54°/0.1 mm., with some unreacted dihydromyrcene and considerable residue. The liquid was *monobromodihydromyrcene* (found: C 55.2; H 7.9; Br 36.5; reactive Br 36.2; I value 226. $C_{10}H_{17}Br$ requires C 55.3; H 7.9; Br 36.8%; I value 234).

Bromination of rubber.—Reaction between *N*-bromosuccinimide (6.6 g., 1 atom Br per two C_5H_8 units) and acetone-extracted crepe rubber (5 g.) in carbon tetrachloride (300 cc.) was complete in 30 min., giving a reddish-brown solution; no hydrogen bromide was liberated. As soon as the reddish-brown, rubberlike product (7.8 g.) was freed from solvent it could not be redissolved; consequently the reactive bromine and the iodine value could not be directly determined. The preparation was therefore repeated in benzene solution, and 10 cc. portions of the solution were taken for these determinations. The bromorubber content of the solution was also determined by evaporation in a vacuum of a 10 cc. portion, the residue being subsequently thoroughly ex-

tracted with methanol (found: C 55.5; H 7.1; Br 37.4; reactive Br 35; I value 155. $C_{10}H_{15}Br$ requires C 55.8; H 7.0; Br 37.2%; I value 236).

The action of bromine on rubber.—A solution of sol rubber (5.0 g.) in chloroform (350 cc.) was cooled to between −30° and −40°, and a solution of bromine (11.8 g., 1.0 mole per C_5H_8 unit) and iodine (0.1 g.) in carbon tetrachloride (100 cc.) was added in the dark, with shaking, in an atmosphere of nitrogen. No hydrogen bromide was evolved during the addition or on bringing the gelled solution to room temperature. The insoluble, pale brown, resinous product (16.5 g.; found: Br 69.0. Calcd. for $C_5H_8Br_2$: Br 70.1%) did not evolve hydrogen bromide at temperatures up to 80°, although it darkened considerably.

Hydrogen bromide was formed in considerable quantity (0.6–0.8 g.) when rubber (5 g.) in carbon tetrachloride or carbon disulfide was treated at 0° with bromine (5.9 g., 0.5 mole per C_5H_8 unit) in the same solvent, under various conditions permitting access or exclusion of light, moisture, and oxygen. When either chloroform or carbon tetrachloride containing alcohol (1%) was used as solvent, no hydrogen bromide was liberated. The most rapid bromination took place in chloroform; moreover, there was no separation of the brominated product, even when a full molecular proportion of bromine per C_5H_8 unit was added. No change in I value and no liberation of hydrogen bromide were observed on heating solutions of partly brominated rubbers (0.5–0.8 mole of bromine per C_5H_8 unit) at 80° for an hour.

For a rapid estimation of rubber hydrocarbon, the sample (acetone-extracted crepe rubber, 0.1 g.) was dissolved in chloroform (50 cc.) and cooled to 0°. Approximately twice the theoretical quantity of bromine was added in chloroform solution of known concentration, and the excess was estimated by treatment with potassium iodide solution, followed by volumetric estimation of the liberated iodine (found: I value by bromine addition, 357; I value by Kemp's modification of the Wijs procedure, 360).

Corrigendum.—The fraction, b. p. 56–60°/0.01 mm., obtained by the chlorination of 1-methylcyclohexene[1] was mainly trichloromethylcyclohexane (found: Cl 49.9. Calcd. for $C_7H_{11}Cl_3$: Cl 50.2%) and not methylcyclohexene dichloride as formerly assumed.

SUMMARY

The chlorination of cyclohexene by chlorine or by sulfuryl chloride (in the absence of a peroxide catalyst) yields substituted as well as additive chlorination products, and the former retain in full the original olefinic unsaturation, as indicated by iodine-value determination; but whereas sulfuryl chloride forms only the additive dichloride and a monochloroölefin which is substituted exclusively in the 3-position, chlorine yields a mixture of saturated trichloro derivative (chloro-substituted addition product) and isomeric monochloroolefins (3- and 4-substituted), with some additive dichloride.

No evidence of substitution at the ethylenic methine carbon atom has been obtained in the chlorination of cyclohexene, dihydromyrcene, and rubber by chlorine. The diminished unsaturation of the chloro-substitution products of the last two hydrocarbons is attributed to cyclization—a process which is complete in the case of rubber, but affects only a minor proportion of the molecules of dihydromyrcene. The same cyclizing tendency appears in the substitutive bromination of rubber by *N*-bromosuccinimide, but not to any appreciable extent in the similar bromination of dihydromyrcene.

Additive chlorination products are formed when rubber is brought into

reaction with chlorine liberated by the thermal dissociation of phenyliodo-dichloride, or of sulfuryl chloride in the presence of a peroxide. The mode of reaction of bromine with rubber, about which many contradictory statements have been made, is found to be entirely additive if the solvent contains a trace of alcohol and the temperature is 0°. A method based on bromine addition may be used for estimating rubber hydrocarbon. Additive bromo and chloroderivatives of rubber are comparatively stable, and give no indication of the spontaneous elimination of halogen acid, either through cyclization reactions or the reformation of double bonds at temperatures up to 80°.

The provision of chlorine in free-radical form appears to be an essential condition for obtaining the wholly additive chlorination of rubber and allied olefins. The reaction of molecular chlorine or bromine, on the other hand, follows a course which can be adequately explained by the initial formation of an activated dihalide, the fate of which is determined by the nature of the olefinic system and the experimental conditions.

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REFERENCES

[1] Bloomfield, *J. Chem. Soc.* **1943**, 289; RUBBER CHEM. TECH. **17**, 1 (1944).
[2] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Ann.* **551**, 80 (1942).
[3] Kharasch and Brown, *J. Am. Chem. Soc.* **61**, 3432 (1939).
[4] See the table which follows. Additive dichlorides were comparatively stable to the silver nitrate reagent.
[5] The lability of substituted bromine toward alcoholic silver nitrate is, however, no certain criterion of the absence of substitution in the β-position, for, in contrast to the anticipated behavior of the halogen in 4-chlorocyclohexene, bromine located in the β- (or 4-) position may quite well be labile, since the halogen in bromocyclohexane, unlike that in chlorocyclohexane, is wholly reactive toward alcoholic silver nitrate.
[6] Kharasch and his collaborators, *J. Am. Chem. Soc.* **61**, 3089 (1939); **62**, 925, 2393 (1940).
[7] Friese and Djiang, *Ber.* **71**, 667 (1938).
[8] Farmer and Sundralingam, *J. Chem. Soc.* **1942**, 121.
[9] Compare the decomposition of ethyl chloride in the presence of chlorine (Rust and Vaughan, *J. Org. Chem.* **5**, 449 (1940).
[10] Anantakrishnan and Venkataraman, *Chem. Rev.* **33**, 27 (1943).
[11] Bloomfield, *J. Chem. Soc.* **1943**, 289; RUBBER CHEM. TECH. **17**, 1 (1944); scheme (2).
[12] Garvey, Halley and Allen, *J. Am. Chem. Soc.* **59**, 1827 (1937).
[13] Kharasch and Brown, *J. Am. Chem. Soc.* **61**, 2142 (1939).
[14] Gladstone and Hibbert, *J. Chem. Soc.* **53**, 682 (1888); Weber, *Ber.* **33**, 786, (1900).
[15] Weber, *Ber.* **33**, 786 (1900).
[16] Hinrichsen and Kindscher, *Z. anorg. Chem.* **81**, 70 (1913).
[17] Kemp, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
[18] Schimmel's Report, Oct. **1911**, p. 128.
[19] Kharasch and Brown, *J. Am. Chem. Soc.* **62**, 925 (1940).
[20] Schumacher and Stauff, *Angew. Chem.* **49**, 613 (1936); **53**, 501 (1940); *Z. Elektrochem.* **48**, 271, 550 (1942).
[21] Michael and Garner, *Ber.* **34**, 4046 (1901).
[22] Markownikow, *Ann.* **152**, 241 (1870); Wolffstein and Rolle, *Ber.* **41**, 733 (1908).
[23] Zappi and Degiorgi, *Bull. soc. chim.* **49**, 1035 (1931); **51**, 1605 (1932).
[24] Farmer, Koch and Sutton, *J. Chem. Soc.* **1943**, 541.
[25] The microanalyses were carried out by W. T. Chambers and (Miss) H. Rhodes.
[26] Bloomfield, *J. Chem. Soc.* **1943**, 289; RUBBER CHEM. TECH. **17**, 1 (1944), Figure 1.
[27] Skita, and Ritter, *Ber.* **44**, 674 (1911).
[28] This was an oxygen-free hydrocarbon obtained by light-petroleum extraction of acetone-extracted crepe rubber, from which the oxygenated fraction had been removed (cf. Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).
[29] Stewart and collaborators, *J. Am. Chem. Soc.* **51**, 3082 (1929).
[30] Compare chlorides of alkyl sulfites (Stähler and Schirm, *Ber.* **44**, 319 (1911)).

RUBBER, POLYISOPRENES, AND ALLIED COMPOUNDS

VII. ACTION OF NITRIC OXIDE*

GEORGE F. BLOOMFIELD AND G. A. JEFFREY

Although the reactions of nitrogen dioxide, dinitrogen trioxide, and nitrosyl chloride with olefins have been studied extensively, the action of nitric oxide has received but little attention, and it has in fact been stated[1] that it does not combine with a normal ethylenic linkage. Nitric oxide is, however, of well established utility in the study of free-radical reactions, which it can promote, retard, or inhibit, in virtue of its property of starting reaction chains, or stopping them by combination with other free radicals.

General characteristics of the reaction of nitric oxide with olefins.—Characteristics of a free-radical mechanism were exhibited. For instance, when a solution of rubber, dihydromyrcene, 1-methylcyclohexene, or cyclohexene was shaken in contact with nitric oxide, there was generally an induction period of 15–30 minutes, depending on the intensity of the prevailing light, before any sign of reaction became evident. Then the solution acquired a pronounced green color, absorption of nitric oxide commenced, and some heat was evolved. The induction period was not confined to the initial starting of the reaction, for if the reaction was stopped by removing the nitric oxide from the system and then, after a short interval, nitric oxide was readmitted, an induction period was again observed before reaction recommenced. Under the conditions employed, the reaction ceased, owing to admixture by nitrogen produced in the reaction. When provision was made for removing the nitrogen, no difficulty was experienced in carrying the reaction as far as was desired, and it became obvious that absorption of nitric oxide could proceed far beyond one molecular proportion per double bond, and that the volume of nitrogen formed was generally between a third and a quarter of the volume of nitric oxide which had been absorbed at any given stage of the reaction. The formation of nitrogen in reactions of nitric oxide with free radicals (but not with olefins) has been reported by Nauta and Mulder[2] and by Sonneborn and Wiselogle[3], who attributed its formation to decomposition of an intermediate hyponitrite.

Obviously the reaction of nitric oxide with olefins does not proceed by any simple attachment of nitric oxide itself to the unsaturated molecule, and it is not surprising that a variety of products was isolated containing nitrogen in various states of combination with oxygen.

Reaction with rubber.—Gorgas's observation[4] that an insoluble nitrogenous product was precipitated by the action of nitric oxide on a rubber solution has been confirmed. This occurred at a stage represented by the absorption of approximately 1 mole of nitric oxide per C_5H_8 unit, and the composition of the product corresponded with the introduction into half of the available C_5H_8 units of groups containing nitrogen and oxygen in the ratio 1:2 to 1:2.7, varying from one preparation to another. At a somewhat earlier stage the

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product could be separated into two components of approximate compositions $C_{10}H_{15}O_2N$ and $C_{10}H_{15}O_3N$. In the early stages of reaction there was considerable reduction of molecular size, by an obscure mechanism which required the absorption of a proportion of nitric oxide appreciably greater than the proportion of oxygen required to bring about a comparable reduction in molecular size.[5]

Reaction with simpler olefins allied to rubber.—Dihydromyrcene and 1-methylcyclohexene yielded products which appeared to contain substituent nitro groups, together with substances of rather lower oxygen:nitrogen ratio. In the formation of the former products the unsaturation was considerably affected, being much lower than that calculated for simple nitro-substituted olefins.

Cyclohexene yielded the following products: (1) the already known crystalline cyclohexene pseudonitrosite[6], (2) a mixture of isomeric nitrocyclohexenes containing a considerable proportion of 1-nitrocyclohexene, and (3) an unstable, nondistillable, viscous oil constituting the major product. Partial separation of the isomeric nitrocyclohexenes yielded a fairly pure sample of the 1-nitro isomer, but the other isomer, in all probability 3-nitrocyclohexene, could not be isolated in a pure state, since it underwent considerable decomposition in the presence of alkali.[7]. The constitution of the 1-nitrocyclohexene was established by oxidation to adipic acid and by reduction to cyclohexanoneoxime, the latter reaction probably proceeding through the intermediate cyclohexenylhydroxylamine (cf. the reduction of nitrocyclohexane to cyclohexylhydroxylamine), or possibly by direct 1:4-addition of hydrogen to the C:C·N:O system. As was expected from the presence on the ethylenic carbon atom of a strongly polar group, capable of forming a conjugated system with the ethylenic linkage, addition of iodine chloride to the $>C{=}C<$ bond was almost completely inhibited, but the additive capacity for hydrogen established the presence of the ethylenic linkage. Spectrographic examination[8] has confirmed the presence of considerable conjugation in the 1-nitrocyclohexene component of the mixture (Figure 1). The other nitrocyclohexene which was present exhibited a much more satisfactory additive capacity for iodine chloride. The constitution of the major nonvolatile reaction product has not been established; it was a unimolecular substance, exhibiting no additive capacity for iodine chloride, with groups containing oxygen and nitrogen in a ratio slightly in excess of 2:1 added or substituted at the original ethylenic linkage of the cyclohexene; treatment with alkali gave a crystalline product of higher nitrogen content than the original oil, suggesting the presence of stable carbon-nitrogen linkages.

The principal characteristics of the reaction under consideration are therefore: (1) various products are formed; all contain nitrogen directly linked to carbon, and the nitrogen is combined with oxygen in the proportion 1:2, 2:3, or 1:3; several of the products are identical with those known to be formed by the action of higher oxides of nitrogen on the corresponding olefin; (2) at least 1 mole of nitrogen is formed for every 4 moles of nitric oxide reacting; (3) when substitutive reaction is taken into account, the H:C ratio is substantially preserved; (4) the ethylenic carbon atoms are extensively involved in substitutive and additive reactions, and (5) the reaction is inhibited by alcohol or acetic acid.

Since most of the reaction products are precisely those obtained by the action of higher oxides of nitrogen or of nitrous acid, it is likely that reaction proceeds by conversion of the nitric oxide into a higher state of oxidation, probably by a free-radical chain mechanism involving the hydrocarbon. The attack at the ethylenic carbon atoms may be closely related to the preferential attack

of free halogen radicals at these carbon atoms[9]. Any such reaction must occur in the liquid phase, since brown fumes in the gas phase were not observed; the presence of nitrous acid or, more probably, dinitrogen trioxide in the liquid phase was, however, detected by Sonneborn and Wiselogle's procedure[3] during the course of the reaction. If nitrous acid itself is formed, it must become involved in a course of reaction other than the usual formation of ψ-nitroles with those secondary nitro groups already present. The formation of some of the

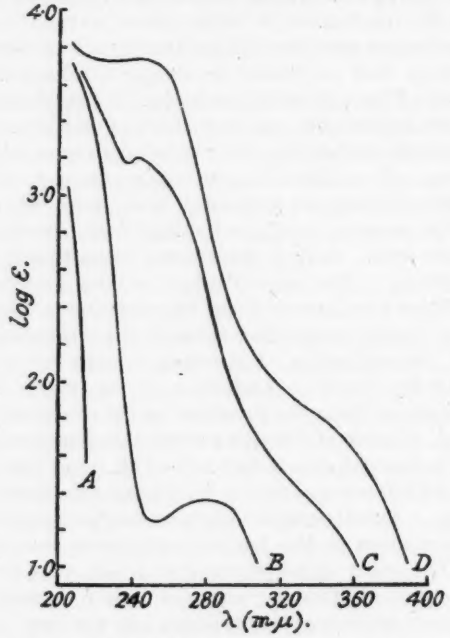

FIG. 1.—*A.*—cyclohexene. *B.*—Nitrocyclohexane. *C.*—Mixture of isomeric nitrocyclohexenes. *D.*—1-Nitrocyclohexene (mainly).

reaction products is satisfied by overall reactions of the type represented by the equations:

$$(a)\ RH + 4NO = RNO_2 + N_2 + HNO_2 \text{ or}$$
$$2RH + 8NO = 2RNO_2 + 2N_2 + N_2O_3 + H_2O$$

$$(b)\ >C{:}C< + N_2O_3 = >C(NO)\cdot C(NO_2)<$$

$$(c)\ 2RH + 10NO = 2RNO_3 + 3N_2 + 2HNO_2 \text{ or}$$
$$2RH + 10NO = 2RNO_3 + 3N_2 + N_2O_3 + H_2O.$$

EXPERIMENTAL[10]

Reactions were conducted either in a glass globe or in a small flask fitted with a sintered-glass distributor through which gas could be passed, first from reservoir *A* into reservoir *B* (Figure 2), and then back into *A* by manipulation of the stopcocks and application of nitrogen pressure to the reservoirs. The

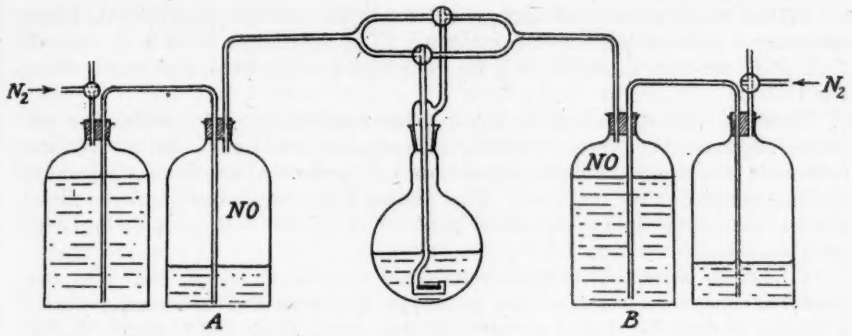

FIG. 2

apparatus was first swept out with purified nitrogen, then evacuated until the solvent had boild vigorously for a few minutes under the reduced pressure, refilled with nitrogen, reëvacuated, and finally filled with nitric oxide obtained from sodium nitrite, potassium ferrocyanide, and acetic acid. The gas remaining at the conclusion of an experiment was displaced into a measuring system and, after removal of any nitric oxide with aqueous potassium permanganate, the volume of residual nitrogen was measured.

Experiments with rubber.—The hydrocarbon (sol rubber, 5 g.) was dissolved in carbon tetrachloride (300 cc.); reaction required 30–120 min. The results are in the table.

REACTION OF NITRIC OXIDE WITH RUBBER

NO consumed (moles per C_5H_8 unit)	N_2 formed (moles per mole NO)	Analysis of product (percentages) C	H	N	O	I value	Solubility of product
0.13	—	84.2	11.3	—	—	—	Soluble
0.15	0.28	83.9	11.3	1.65	3.2	—	Soluble*
0.19	0.23	83.15	11.1	—	—	—	Soluble
0.48	0.25	76.0	10.15	4.2	9.65	262	Soluble†
0.94	0.24‡	—	—	—	—	—	Soluble
0.95	0.29	68.7	9.05	6.0	16.25	220	Partly insoluble
ca. 1.0	—	63.25	8.45	7.85	20.3	—	Insoluble
ca. 0.9	—	68.0	8.9	6.95	16.15§	—	Insoluble part, 74% of product
		60.7	7.85	6.85	24.6‖	—	Soluble part, 26% of product
1.35	0.29‡	—	—	—	—	—	Insoluble

* Intrinsic viscosity 0.74 in benzene +15% methanol; mol. wt. 74,000 (original mol. wt. 238,000).
† Intrinsic viscosity 0.57 in benzene; mol. wt. 33,000 (original mol. wt. 220,000).
‡ In these experiments the absence of carbon dioxide in the residual gas was demonstrated by passage of the latter through a weighed CO_2-absorption tube.
§ Empirical formula $C_{10}H_{15.6}(NO_2)_{0.9}$. ‖ Empirical formula $C_{10}H_{15.4}NO_3$.

Experiments with dihydromyrcene and 1-methylcyclohexene.—Dihydromyrcene (15.6 g.) in carbon tetrachloride (150 cc.) was shaken with nitric oxide (1888 cc., N.T.P.) in the glass globe during 8 hours in diffused sunlight. The residual gas (588 cc.) contained a little nitric oxide (38 cc.), whence the nitric oxide consumed and the nitrogen formed were equivalent to 0.73 mole and 0.22 mole, respectively, per mole of dihydromyrcene. A little yellow resin was precipitated. The yellow supernatant solution yielded on distillation unreacted dihydromyrcene (10.8 g.), a liquid fraction, b. p. 66–70°/0.001 mm. (0.6 g.), and considerable residue (4.1 g.; found: C 55.55; H 8.5; N 11.6%; I value 79, corresponding to $C_{10}H_{18}O_{3.3}N_{1.8}$). The liquid fraction was probably a *nitrodihydromyrcene* [found: C 65.6; H 9.4; N 7.7; I value 156. $C_{10}H_{17}O_2N$ requires C 65.5; H 9.35; N 7.65%; I value 277 (I_2^-), 139 (I_1^-)].

1-Methylcyclohexene similarly yielded a liquid product, b. p. 50°/0.01 mm., probably a *nitromethylcyclohexene* (found: C 59.3; H 8.0; N 10.0; I value 73. $C_7H_{11}O_2N$ requires C 59.55; H 7.85; N 9.9%; I value 180), and some viscous residue.

Reaction with cyclohexene.—Nitric oxide equivalent to 1.6 moles per mol. of cyclohexene was consumed during 15 hours in a dull light, with formation of 0.44 mole of nitrogen; a white, crystalline solid separated continuously from the commencement of the reaction. This (2.44 g.) was filtered off, and the filtrate yielded on distillation a pale yellow liquid, b. p. 33–46°/0.01 mm. (about 6 g.), and considerable residue (14.4 g.).

Crystalline solid.—This was cyclohexene ψ-nitrosite, m. p. 153° (decomp.) from benzene, mixed m. p. with authentic specimen 153° (decomp.) (found: C 45.55; H 6.35; N 17.5; I value 0. Calcd. for $C_6H_{10}N_2O_3$: C 45.55; H 6.35; N 17.75%); recrystallization from chloroform-alcohol separated it into triclinic needles, m. p. 153° (decomp.), $d_4^{20°}$ 1.389, and monoclinic prisms, m. p. 153° (decomp.), $d_4^{20°}$ 1.378.

Note on crystal structure of cyclohexene nitrosites (by G. A. Jeffrey).—The triclinic needles had cell dimensions: $a = 7.19$ A., $b = 10.20$ A., $c = 5.15$ A., $\alpha = 90°$, $\gamma = 98°$, $\beta = 104.5°$, whence the calculated density for $2(C_6H_{10}N_2O_3)$ was 1.35. The space group may be $P1$, with an asymmetric dimeric molecule, or $P\bar{1}$ with two monomers or one centrosymmetric dimer. These dimensions, particularly the short c axis, impose certain limitations on the choice of possible configurations for this compound. About 3.3 A. being allowed as the nearest approach of atoms in adjacent molecules, between which there are only ordinary van der Waals forces, it follows that the width of the molecules along any line parallel to the c axis must not exceed about 2.2 A. For the monomeric nitrosite, there are a number of configurations to consider, depending on the positions of the NO_2 and NOH groups and the shape of the ring. Two such arrangements, one with a Sachse boat-shaped ring and the other with the chair-shaped ring, would give the necessary flat molecules, but neither of these could be packed into the unit cell without a much closer association than 3 A. between atoms of adjacent molecules. The triclinic form must therefore be dimeric.

The monoclinic prisms had cell dimensions: $a = 11.44$ A., $b = 12.28$ A., $c = 11.06$ A., $\beta = 101°21'$; whence the density calculated for 4 dimeric or 8 monomeric molecules in the cell was 1.36. The space-group was $P2_1/c$. Although the cell dimensions give little guide to the molecular shape, there is scarcely sufficient room to accommodate eight monomeric molecules and four dimers seems the more likely.

Consideration of the configurations for the dimeric molecules is complicated by uncertainty of the true nature of the associating link[11]. For the triclinic form, only a molecule with the C–N (nitro) vonds approximately in the plane of the ring is consistent with the short axis, and for the monoclinic prisms a stereoisomeric arrangement with the nitro group projecting out of the plane is possible.

Liquid product.—This appeared to be a mixture of isomeric nitrocyclohexenes (found: C 56.6; H 7.15; N 11.3; I value 75. Calcd. for $C_6H_9O_2N$: C 56.7; H 7.15; N 11.0%; I value 200), the presence of the nitro group being indicated by the following facts: (1) Close resemblance to authentic nitrocyclohexenes prepared by two different methods (see below). (2) The blue color characterizing a secondary nitro group was observed on treatment with nitrous acid. (3) The active hydrogen content (*ca.* 0.1%), which probably arose from

partial isomerization of the nitro group, was much too low to permit of the presence of a hydroxyl group. (4) No derivatives characterizing a carbonyl or a hydroxyl group could be obtained. (5) *Cyclohexyl nitrite* (found: C 56.2; H 8.8; N 10.8. $C_6H_{11}O_2N$ requires C 55.74; H 8.6; N 10.8%, prepared by the action of nitrous acid on cyclohexanol, had a considerably lower b. p. (<30°/13 mm., 41°/20 mm.) than the liquid under consideration. (6) Reduction with zinc dust in acetic acid gave a 30% yield of cyclohexanoneoxime, m. p. 75–79°, mixed m. p. with authentic specimen (m. p. 84–85°) 79–81° (found: C 63.1; H 9.65; N 12.3. Calcd. for $C_6H_{11}ON$: C 63.2; H 9.7; N 12.3%). Reduction of nitrocyclohexane under the same conditions yielded *cyclohexylhydroxylamine*, m. p. 137° (found: C 62.6; H 11.4; N 12.1. $C_6H_{13}ON$ requires C 62.55; H 11.4; N 12.15%), which was sparingly soluble in water (solution feebly alkaline). (7) Hydrogen uptake was 7 atoms per mole with Adams's catalyst, 8 atoms per mole with Raney nickel. (8) The ultraviolet absorption spectrum (curve *C*, Figure 1) established the presence of considerable conjugation. (9) To 3.4 g. of the liquid, stirred with 2 *N* sodium hydroxide (14 cc.), was added a 3% solution of potassium permanganate (315 cc.) at 0–20°; the yield (1.3 g.) of adipic acid, m. p. 151°, mixed m. p. 151° (found: c 49.5; H 6.95; equiv., 73. Calcd. for $C_6H_{10}O_4$: C 49.3; H 6.9%; equiv., 73), established the presence of at least 40% of 1-nitrocyclohexene in the sample. (10) 1-Nitrocyclohexene was partly separated from the accompanying isomer by shaking with cold *N* sodium hydroxide, in which 1-nitrocyclohexene was known to be insoluble, and then extracted with ether. The alkali-insoluble portion had b. p. 35–36°/0.01 mm., and 1.0 g. gave 0.8 g. of adipic acid (equivalent to 0.7 g. of nitrocyclohexene) on oxidation as above; (found: C 56.65; H 7.3; N 10.7%; I value 23). (For ultraviolet absorption spectrum see curve *D*, Figure 1.) The alkali-soluble portion, b. p. 30–42°/0.01 mm., had undergone partial hydrolysis[12] [found: C 61.2; H 7.7; N 8.5; I value 119. Calcd. for mixture of 75% $C_6H_9 \cdot NO_2$ and 25% $C_6H_9 \cdot OH$ (?): C 60.9; H 7.7; N 8.5%; I value 215].

Examination of other specimens of nitrocyclohexene.—1-Nitrocyclohexene, b. p. 45–50°/0.1 mm. (found: C 56.0; H 7.53; N 10.8%; I value 29), prepared according to Wieland[13], was insoluble in *N* sodium hydroxide; 1.9 g. gave 1.1 g. of adipic acid on oxidation, and the hydrogen uptake (Adams's catalyst) was 7 atoms per mole 3(?)-Nitrocyclohexene, b. p. 34°/0.01 mm. (found: C 56.25; H 7.1; N 10.9%; I value 155), prepared by the action of alkali on cyclohexene ψ-nitrosite[13] was soluble (with partial hydrolysis) in *N* sodium hydroxide; 0.8 g. gave 0.15 g. of adipic acid, corresponding to the presence of 16% 1-nitrocyclohexene, and the hydrogen uptake (Adams's catalyst) was 7.5 atoms per mole.

Residue.—This slowly decomposed at room temperature, and could not be distilled without severe decomposition. An effective separation from cyclohexene ψ-nitrosite was achieved by dissolution in methanol at 0°, in which the nitrosite was insoluble; removal of the alcohol gave a brown viscous oil. The products of four separate reactions were remarkably constant in composition [found: C 44.6 ± 0.5; H 6.1 ± 0.1; N 13.9 ± 0.1%; I value 4; *M* (f. p. depression in benzene), 164], which corresponded to the formula $C_5H_{10}O_{3.6}N_{1.6}$. Oxidation of 4.6 g. with alkaline permanganate (3%, 270 cc.) proceeded only slowly and yielded an unidentified neutral oil (0.55 g.) and adipic acid (1.7 g.). Oil (5.4 g.) in alcoholic potassium hydroxide (100 cc., 0.82 *N*) at the b. p. for 15 min. yielded a large and a small portion, respectively, soluble and insoluble in alkali. Distillation of the former yielded a little impure nitrocyclohexene, b. p. 40–47°/0.1 mm. (found: C 57.1; H 7.4; N 10.6. Calcd. for mixture of

96.75% $C_6H_9 \cdot NO_2$ and 3.25% $C_6H_9 \cdot OH$: C 57.15; H 7.25; N 10.5%), and a considerable residue from which an unidentified crystalline *solid* separated, m. p. 107–108° from benzene (found: C 46.0; H 5.15; N 17.7. $C_6H_8O_3N_2$ requires C 46.1; H 5.15; N 17.95%).

The reaction of nitric oxide with cyclohexene did not proceed in alcoholic solution, or in a medium containing acetic acid. Nitric oxide did not react with nitrocyclohexene in carbon tetrachloride.

SUMMARY

The reaction of nitric oxide with the olefins cyclohexene, 1-methylcyclohexene, dihydromyrcene, and rubber presents characteristics of a free-radical, chain reaction. In the products, the molecular ratio of combined oxygen to nitrogen is considerably in excess of 1:1, the nitrogen atom being generally directly linked to carbon. In many instances definite nitro compounds have been isolated, and a considerable part of the attack appears to proceed at the ethylenic carbon atoms, either by substitution or addition of NO_2 and N_2O_3 groups. The precise reaction mechanism is obscure.

ACKNOWLEDGMENT

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REFERENCES

[1] Sidgwick, "The Organic Chemistry of Nitrogen", 1937, p. 213.
[2] Nauta and Mulder, *Rec. trav. chim.* **58**, 1070 (1939).
[3] Sonneborn and Wiselogle, *J. Am. Chem. Soc.* **64**, 860 (1942).
[4] Gorgas, *Ber.* **63**, 2700 (1930).
[5] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, 125.
[6] Baeyer, *Ann.* **278**, 110 (1894); Wieland, *Ann.* **424**, 71 (1921).
[7] Compare the instability of α-methylene-substituted halogen; see preceding paper.
[8] By H. P. Koch, for which the authors' thanks are due.
[9] See preceding paper (this issue).
[10] The microanalyses were carried out by W. T. Chambers and (Miss) H. Rhodes.
[11] Sidgwick, "The Organic Chemistry of Nitrogen", 1937, p. 214.
[12] A high order of reactivity of groups substituted at the 3-position of cyclohexene has already been observed in halogen-substitution products (cf. preceding paper in this paper).
[13] Wieland, *Ann.* **424**, 71 (1921).

THE STATISTICAL LENGTH OF RUBBER MOLECULES*

L. R. G. TRELOAR

The general methods described in a previous paper[1] for the calculation of the statistical lengths of paraffin molecules may be applied also to the problem of the rubber (polyisoprene) molecule, though on account of its less simple geometrical structure the detailed calculations are rather more elaborate. Thus, every fourth linkage between the carbon atoms is a double bond which is known from chemical evidence not to permit of rotation of the adjacent single bonds. The main chain of carbon atoms is, therefore, made up of a series of rotating and nonrotating links. It is generally believed that the single bonds adjacent to the double bonds are in the *cis* position in rubber. The chain structure is, therefore, of the form shown in Figure 1 (*a*), representing two isoprene units.

THE EQUIVALENT GEOMETRICAL CHAIN

Instead of dealing with the system in its original form it is desirable to construct an equivalent geometrical chain which is more amenable to treatment. The condition of rigidity of the double bond requires that the bonds 1 and 3 are always in the same plane, and on the same side of 2. Suppose AB and DC are produced to meet in E. The original system ABCD may clearly be replaced by the geometrical links AE and ED, such that ED is free to rotate about AE at the fixed angle γ. Taking $\angle ABC = 125.25°$:

$$AB = CD = DA' = 1.54 \text{ A}$$

and BC = 1.34 A, the length of AE is 2.70 A, and the angle γ is $109\frac{1}{2}°$. The angle α between the single bonds is assumed to be $70\frac{1}{2}°$, as in the paraffin chain, so:

$$\gamma = 180° - \alpha$$

The original chain may, therefore, be replaced by an equivalent system of freely-rotating geometrical links, of which the repeating unit consists of two links each of length 2.70 A at an angle of $109\frac{1}{2}°$ and one link of length 1.54 A at an angle of $70\frac{1}{2}°$ (Figure 1(*b*)).

In the problem of the paraffin molecule, the effects of the valence angle were accurately taken into account up to the 5-link chain. The higher-membered chains were built up by considering 5-link chains to be joined in a random manner, without regard to valence angles. For the rubber molecule, it is not possible to carry the accurate treatment as far as five (geometrical) links, because the 5-link rubber chain is able to fold over and cross itself, while in the paraffin chain this possibility occurs only when the number of links exceeds 5. The accurate consideration of the valence angles in the rubber

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problem is carried as far as the 4-link chain; thereafter the 4-link chains are combined at random.

Unfortunately the 4-link chain does not form a repeating unit. From Figure 1 (*c*) it is seen that, proceeding along the chain, two types of 4-link systems are encountered. If these are denoted by A and B, the chain is built up of a succession of two B's and one A. The shortest repeating unit which can be formed is the 12-link system BBA, equivalent to 4 isoprene units.

From this analysis the procedure actually followed in building up the higher-membered chains will be understood. First, curves were derived to represent accurately the length distribution for each of the 4-link systems A

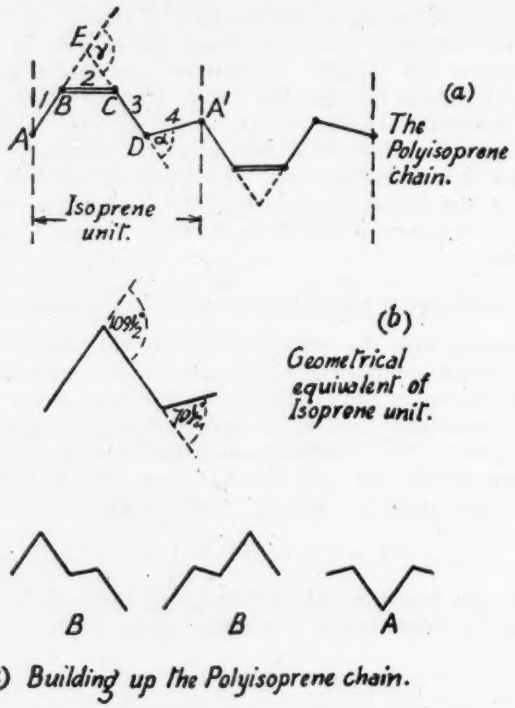

FIG. 1.—(*a*) The polyisoprene chain (methyl side groups omitted). (*b*) Geometrical equivalent of isoprene unit. (*c*) Building up the polyisoprene chain.

and B. This derivation was carried out partly by graphical methods, in just the same way as for the 4-link paraffin. Next, the distribution function for two type-B systems joined at random was obtained. The resultant 8-link system BB was then combined in a random manner with the 4-link system A, leading to a 12-link chain, BBA. This chain—subsequently referred to as the "4-isoprene unit"—forms the basic unit from which the higher chain distributions were obtained by simple combination, in exactly the same way as for the higher paraffin chains[2].

In the following paragraphs the steps in the procedure will be discussed in more detail, together with the numerical results. The derivation of the mathematical relations utilized is given in the appendices.

THE 4-ISOPRENE UNIT

The first step is to obtain the distribution functions for the A and B types of 4-link chain. These will be considered in turn.

4-link Type A.—As in the case of the 4-link paraffin chain, it is necessary first to derive the angular distribution function for two links rotating about an axis. Figure 2 represents the rotation of one short link BL and one long link

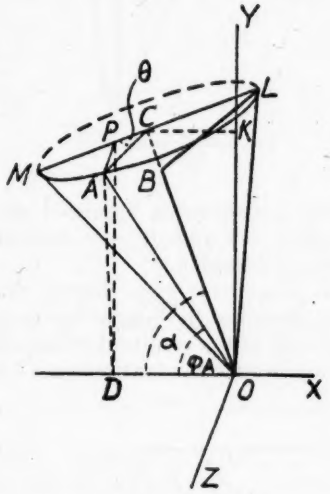

FIG. 2.—The ϕ_A distribution function.

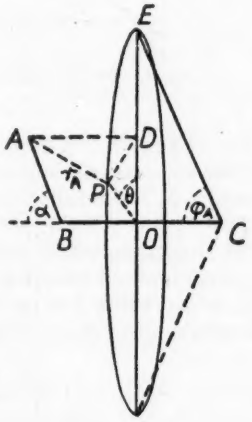

FIG. 3.—The 4-link chain type A.

OB about the axis DOX, the angles BOX and LBO being $109\frac{1}{2}°$ $(\pi - \alpha)$. If ϕ_A is the angle between the moving line OA and OD, the distribution function for ϕ_A, in the integral form, is found to be (Appendix 1):

$$\int_0^{\phi} p_1(\phi_A)d\phi = \frac{1}{\pi} \text{arc cos } (2.58 \cos \phi - 0.78) \qquad (1)$$

The distribution of length r of the 4-link chain of type A is obtained by considering the two links AB and BC to be fixed, while the third and fourth links are represented by the vector CE making the angle ϕ_A with BC (Figure 3). If r_A is the distance AP (where P is the instantaneous position of E) in Angstrom units, the distribution function for the r_A values corresponding to a given (elementary) value of ϕ_A is (Appendix 3):

$$\int_{r_0}^{r} p_2(r_A)dr = \frac{1}{\pi} \text{arc cos} \left(\frac{24.8 - 22.6 \cos \phi_A - r^2}{10.4 \sin \phi_A} \right) \qquad (2)$$

The total distribution $p(r_A)$ is obtained by dividing up the ϕ_A-function into elements, drawing the respective curves, and adding up the ordinates at successive values of abscissa r_A.

The resulting form of the integral distribution function $\int p(r_A)dr$ for the 4-link chain type A is shown in Figure 6.

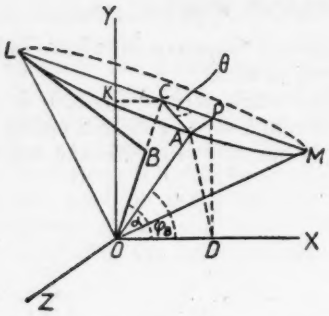

FIG. 4.—The ϕ_B distribution function.

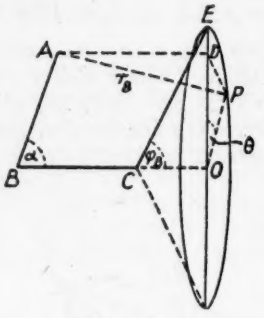

FIG. 5.—The 4-link chain type B.

4-link Type B.—The geometry of this system is shown in Figures 4 and 5, and the expressions corresponding to Equations (1) and (2) are derived in Appendix 2. The function $\int p(r_B)dr$ is shown in Figure 6.

The 12-link Chain.—The distribution of length for two B-type chains joined at random was obtained by the method described in the previous paper[3]. The same method was then applied to the joining of the resultant 8-link (BB) chain to one 4-link A-type chain. The distribution function for the final 12-link (4-isoprene unit) chain is shown in Figure 7.

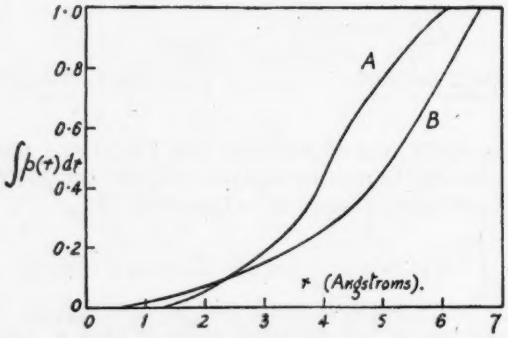

FIG. 6.—Integral distribution functions for the 4-link chains of types A and B.

HIGHER-MEMBERED CHAINS

The higher-membered chains, *i.e.*, of 8 and 16 isoprene units, were obtained by the straightforward application of the procedure already described[3], including the special approximation for the calculation of the exponential "tail" of the distribution curves[4]. The resulting distribution curves are given in Figure 7. The function for the 16-isoprene chain was found to be almost identical with the Gaussian form:

$$p(r) = \frac{4\beta^3}{\pi^{\frac{1}{2}}} r^2 e^{-\beta^2 r^2} \qquad (3)$$

up to $r = 36$ A. It is evident that still higher chains must approximate even

more closely with this form. Hence there is no need to carry out the graphical procedure for the derivation of the main part of the distribution curve; it is only necessary to apply Formula (3), and to halve the parameter β^2 when the number of chain links is doubled. The detailed calculations need be made only

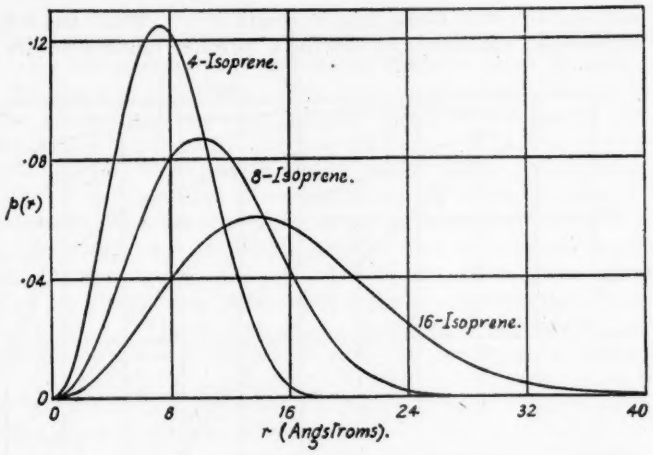

FIG. 7.—Length distribution for chains of 4, 8, and 16 isoprene units.

for the "tail" of the curve, and here the approximate method is applicable. The amount of labor involved in deriving the higher chains is thus considerably reduced. Table I gives the values of β^2 in Equation (3) for chains

TABLE I

VALUES OF β^2 IN EQUATION (3), AND UPPER LIMIT OF r FOR WHICH THIS EQUATION IS VALID, FOR POLYISOPRENE CHAINS OF VARIOUS LENGTHS

No. of isoprene units in chain	β^2	Upper limit of r (A)
16	0.0053	36
32	0.00265	65
64	0.001325	125
128	0.000662	230
256	0.000331	440

from 16 to 256 isoprene units, and the approximate values of r at which the formula ceases to be applicable.

The portions of the distribution curves corresponding to the higher ranges of r are represented in Figure 8. To show the series on a reasonable scale the function $\log_{10} p(r)$, (where $p(r)\delta r$ is the probability of a value of r between r and $r + \delta r$ Angstrom units), is plotted against $(r/r_m)^2$, r_m being the length of the fully extended chain. The broken curve shows for comparison the Formula (3) for the chain of 256-isoprene units. As in the case of the paraffin chains, the actual probability falls increasingly below that calculated from Equation (3) as r approaches r_m.

Accuracy of Data.—The joining of the 4-link chains at random, instead of at a definite angle, leads to certain errors, the magnitude of which will now be considered. First, the length of the 4-isoprene unit, 19.4 A, as derived, differs

from the actual length of the 4-isoprene unit, 18.4 A, projected on to the direction of the fully extended polyisoprene chain. The maximum chain-lengths, r_m, are therefore about 5 per cent too high.

Secondly, the neglect of the valence angle effect on joining the 4-link chains leads to an incorrect value of β in Equation (3), and therefore to an incorrect value of the root mean square length $(\overline{r^2})^{\frac{1}{2}}$. Wall[5] has recently derived an expression, analogous to Eyring's formula relating to the paraffin

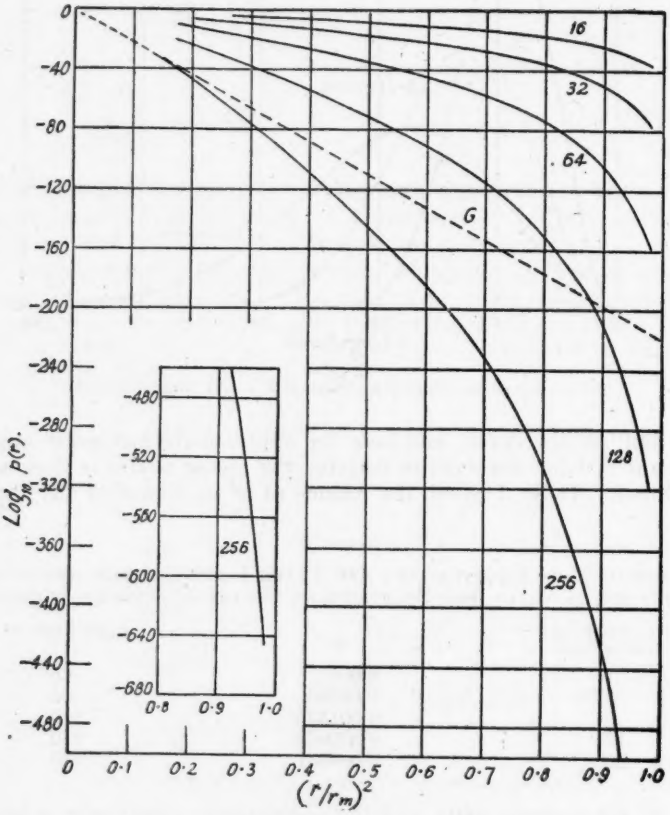

FIG. 8.—Log 10 $p(r)$ for chains of 16, 32, 64, 128 and 256 isoprene units. G represents equation (3) with $\beta^2 = .000331$.

chain, for the root mean square length of a chain of vectors corresponding to the rubber molecule. Insertion of the values of bond lengths and angles assumed in the present paper (which differ slightly from those used by Wall), in Wall's formula, gives for the root mean square value of r:

$$(\overline{r^2})^{\frac{1}{2}} = 1.93n^{\frac{1}{2}}$$

where n is the number of bonds in the rubber chain. There being 4 such bonds per isoprene unit, the value of $(\overline{r^2})^{\frac{1}{2}}$ for the chain of 256 isoprene units

derived from this formula is 61.8 A, which is to be compared with the value of 67.4 A derived from the distribution curve. The difference, +9 per cent, is of the same order of magnitude as that found for the paraffin chain ($\sim -6\%$), though in the opposite sense. The fact that in the present case the calculated r^2 is higher than it should be is due to the presence of two long links which include an angle of less than 90°.

The Trend of the Distribution Functions.—Comparison of the curves of Figure 8 with the data already presented[1] shows a close similarity in form between the two sets of curves. This is to be expected, because the precise form of the geometrical repeating unit of the chain becomes of less and less significance as the length of the chain is increased. The data have been computed up to a chain of 256 isoprene units, equivalent to a molecular weight of 17,400. This is greater than the effective length of the molecules (between points of cross-linkage) usually encountered in vulcanized rubber.

Inspection of the data in Figure 8 shows that the successive curves differ approximately by a factor of 2. That is to say, for a given value of r/r_m, the value of $\log_{10} p(r)$ for a chain of $2n$ links is approximately twice that for a chain of n links. The curves could, therefore, if necessary, be extended upwards to higher chain lengths with sufficient accuracy for many purposes, simply by multiplying by a proportionality factor. It seems probable, therefore, that the function represented in Figure 8 approximates to a constant form as the length of chain is increased.

CONCLUSION

As pointed out in I, the assumption of complete freedom of rotation and the other assumptions inherent in the above statistical method are probably less well satisfied in the case of the actual material, rubber, than in the case of the paraffins. Taking into account the rigidity of the system ABCD (Fig. 1) as well as the presence of the methyl group (not shown) attached to the carbon atom C, it is certain that many theoretically possible positions of rotation of the chain members will be excluded in practice. Nevertheless, the present treatment does represent a step in advance of the position reached by Kuhn, who used the formula (3) to represent the distribution of lengths of the molecules. Though not necessarily quantitatively accurate in their applicability to rubber, the distribution functions derived in the present work do represent the *kind* of deviations from the simple formula which must occur.

The work described in this paper forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

APPENDIX

THE ϕ_A-FUNCTION

In Figure 2, let OB be in the plane YOX, and let A be the position of the point L in the rotation of the short link BL about the long link OB. Let LM be the diameter in the plane YOX of the circle, of centre C, described by L, and let the angle ACM = θ. If CK and AP are perpendicular to OY and LM respectively, and PD is perpendicular to XO produced, then AD is also perpendicular to XO. If ϕ_A is the angle AOD, then:

$$\cos \phi_A = \frac{OD}{OA} = \frac{CK + CP \sin \alpha}{OL} = \frac{CK + CA \sin \alpha \cos \theta}{OL} \qquad (4)$$

Insertion of the values of angles and lengths given in paragraph 2 thus gives:

$$\cos \phi_A = 0.304 + 0.388 \cos \theta$$

whence, by the argument used in the previous paper[5]:

$$\int_{\phi_0}^{\phi} p_1(\phi_A)d\phi = \frac{1}{\pi} \text{arc cos } (2.58 \cos \phi_A - 0.78)$$

THE ϕ_B-FUNCTION

The links OB and BL rotate about the axis OX. The construction (Figure 4) is similar to that for the ϕ_A-function, and the result is deduced in the same way, by insertion of the appropriate values in the expression (4). The result is:

$$\int_{\phi_0}^{\phi} p_3(\phi_B)d\phi = \frac{1}{\pi} \text{arc cos } (1.46_5 \cos \phi - 0.34)$$

THE 4-LINK CHAIN TYPE A

The short link AB (Figure 3) and the long link BC are considered fixed, while the two remaining links are represented by the line CE, of length 3.52 A, rotating about OC at the variable angle ϕ_A. If OE and AB are coplanar, and AD is drawn perpendicular to OE, then, if θ is the angle DOP:

$$r_A^2 = AP^2 = AD^2 + (DO^2 + OP^2 - 2DO \cdot OP \cos \theta) \qquad (5)$$

which, on insertion of the given magnitudes, becomes:

$$r_A^2 = 24.8 - 22.6 \cos \phi_A - 10.4 \sin \phi_A \cos \theta$$

r_A being measured in Angstroms. Hence:

$$\int_{r_0}^{r} p(r_A)dr = \frac{1}{\pi} \text{arc cos } \left(\frac{24.8 - 22.6 \cos \phi_A - r^2}{10.4 \sin \phi_A} \right) \qquad (6)$$

represents the elementary distribution of r_A-values corresponding to a given value of ϕ_A.

THE 4-LINK CHAIN TYPE B

In this case there are two long links AB and BC (Figure 5) considered fixed, and one long and one short link in rotation, represented by CE. Insertion of the appropriate values in (4) gives:

$$r_B^2 = 22.1 + 12.7 \cos \phi_B - 17.9 \sin \phi_B \cos \theta$$

whence the elementary distribution is:

$$\int_{r_0}^{r} p(r_B)dr = \frac{1}{\pi} \text{arc cos } \left(\frac{22.1 + 12.7 \cos \phi_B - r^2}{17.9 \sin \phi_3} \right)$$

SUMMARY

The paper applies the methods worked out for the determination of the statistical lengths of paraffin chains to the more complex problem of the rubber molecule. Distribution functions covering lengths up to 98 per cent of the fully extended length are given for chains corresponding to molecular weights up to 17,400.

REFERENCES

[1] Treloar, *Proc. Phys. Soc.* **55**, 345 (1943).
[2] The calculations do not take account of the modification of the bond structure at the ends of the polyisoprene molecule. For this reason the actual molecule is not exactly the same as that assumed, but the difference is negligible for long chains.
[3] Treloar, *Proc. Phys. Soc.* **55**, 345 (1943); paragraph 9.
[4] Wall, *J. Chem. Physics* **11**, 67 (1943).
[5] Treloar, *Proc. Phys. Soc.* **55**, 345 (1943); Appendix 2.

CHEMISTRY OF SULFUR-OLEFIN REACTIONS

APPLICATION TO VULCANIZATION *

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During recent years there has been general acceptance of the theory that the marked alteration in physical properties of rubber, termed "vulcanization", is a consequence of progressive cross-linking through primary valence bonds. Attempts have been made to place this theory on a quantitative basis in the kinetic theory of elasticity[1]. Accompanying phenomena such as isomerization[2], cyclization[3], and degradation reactions (reversion) may occur, and account for the differences observed under various conditions of vulcanization in the early stages or soft rubber range. These secondary reactions probably become very important in the ebonite stage.

The vulcanization of saturated hydrocarbon polymers, such as polyisobutylene, has been notably unsuccessful in contrast with polyenes, such as natural rubber, drying oils (to produce factice), and butadiene polymers and copolymers. The vulcanization of polychloroprene (or its conversion from α-polymer to μ-polymer in Carothers' terminology[4]) can proceed without the addition of other reactants and is, therefore, distinct in type from the others mentioned.

The difficulties inherent in a direct study of the chemistry of sulfur vulcanization, when rubber itself is used, follow from the fact that, in the commercial range of soft rubber vulcanizates, only from one to six sulfur atoms are combined for each hundred double bonds; also, the product becomes insoluble even before the lower amount has been combined.

In this paper it is proposed, as a working hypothesis, that the chemical reactions which proceed during the vulcanization of natural rubber or diene polymers can be duplicated by the reaction of simple olefins of analogous structure (2-methyl-2-butene or 2-butene) with the vulcanizing agents, and that the pure reaction products have their counterpart in the vulcanizate.

CHARACTER OF OLEFIN–SULFUR REACTIONS

Although vulcanization of rubber by sulfur alone has been superseded in commercial practice by formulations which are much more efficient, it has seemed desirable to study the general nature of the reaction of simple olefins, such as cyclohexene, 5-methyl-4-nonene, and 2-methyl-2-butene, with sulfur alone, in order that the effect of other ingredients in the vulcanization mixture may be better understood.

Dehydrogenation of hydroaromatic compounds with the aid of elementary sulfur (Vesterburg reaction) is usually carried out at relatively high tempera-

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tures, and the mechanism has received little attention. With large proportions of sulfur at high temperatures, a similar reaction occurs with rubber, accompanied by severe degradation. That sulfur may be combined with rubber under conditions such that dehydrogenation is negligible has been shown by Fisher and Schubert[5]; they found by ultimate analysis that a carefully prepared and extracted ebonite possessed a carbon-hydrogen ratio indistinguishable from the theoretical ratio for rubber. This conclusion was further verified in this laboratory by heating large proportions of sulfur with rubber in vacuum and by heating the low-molecular-weight olefin, 5-methyl-4-nonene, with sulfur in a stream of nitrogen. In the range 120° to 140° C, the amount of hydrogen sulfide evolved in either case amounts to much less than 1 per cent of the sulfur combined. These results might be explained by assuming that sulfur simply adds to the double bonds or that hydrogen sulfide is formed and immediately adds to the double bonds under the catalytic influence of sulfur. The latter assumption forms the basis of one theory of vulcanization[6]. By the action of sulfur on alkenes under more severe conditions than those employed in vulcanization, products consistent with such a process are obtained. Jones and Reid[7], in a study of the reaction of sulfur with alkenes, employed temperature-time conditions (10 hours at 180° C) intermediate between those commonly employed for vulcanization and for dehydrogenation. Considerable proportions of carbon, carbon disulfide, and hydrogen sulfide were formed, as well as secondary reaction products of the olefin with hydrogen sulfide—namely, thiols and thio ethers. Meyer and Hohenemser[8] investigated the reaction of cyclohexene with sulfur under temperature conditions approximating those of vulcanization; they isolated cyclohexyl mercaptan, dicyclohexyl sulfide, and high-boiling products which contained sulfur. Here, also, the mercaptan and sulfide presumably result from secondary reactions; obviously an undetermined dehydrogenation must have preceded their formation. In preliminary work in this laboratory, cyclohexene and sulfur were heated at somewhat lower temperatures; only nonvolatile polysulfides [average composition $(C_6H_{10}S_4)_x$, where x was about 3.5] were found. No thiol or thio ether could be detected.

In the reaction of 5-methyl-4-nonene with sulfur at 136° C, the volatile product obtained after several passages through a molecular still (to remove elementary sulfur and nonvolatile products) corresponded in average composition to $C_{20}H_{40}S_{4.5}$. Neither the reaction with cyclohexene nor that with methylnonene was carried to completion, since a large excess of olefin was used and free sulfur remained at the end of the reaction. A considerable proportion of the sulfur contained in both products could be removed by long digestion in a water-acetone solution of sodium sulfite. This reagent is capable of removing sulfur from dialkyl polysulfides, with formation of sodium thiosulfate, and dialkyl disulfides. The products of the reaction of 2-methyl-2-butene with sulfur at 120° C were also polysulfides, which, on treatment with acetone-water solution of sodium sulfite, yielded alkenyl alkyl disulfides in which the alkenyl groups were largely β-methylcrotyl; the alkyl group, though not characterized, must have been either 3-methyl-2-butyl or *tert*-amyl, probably the former (Table II, product 5, and Table III, product 5*b*). The high sulfur content of the initial products, even in the presence of a large excess of olefin, suggested that a similar phenomenon might be observed in rubber. Numajiri[9] showed that, with very high proportions of sulfur, an ebonite is obtained in which the combined sulfur far exceeds that corresponding to one atom of sulfur per isopentene segment. How much, if any, of this sulfur is in the form of polysulfides remains undetermined.

From this preliminary work it may be concluded that, at moderate temperatures, sulfur combines with olefins without degradation or elimination of hydrogen sulfide and establishes "cross-links", apparently consisting of polysulfides, between the monoölefin molecules. (The inefficiency of simple rubber-sulfur vulcanization, when compared with vulcanization by modern formulations, cannot be attributed entirely to ineffective polysulfide sulfur. This inefficiency is probably due also to a larger proportion of sulfur in cyclized structures or to differences in distribution.)

REACTANTS FOR EFFICIENT RUBBER COMPOUNDING

Of the many variables which characterize rubber compounding, it was first desirable to isolate those essential to the most efficient cross-linking. A large amount of rubber compounding[10] has been directed toward the identification

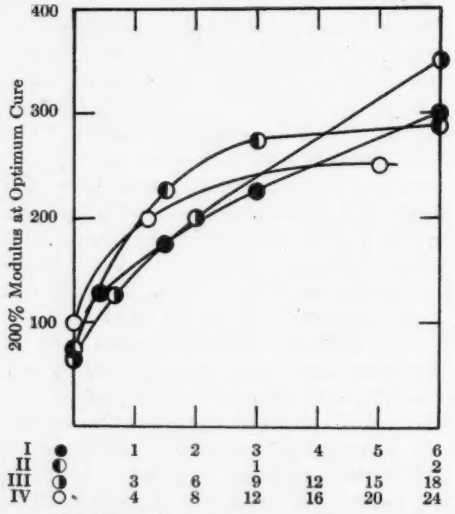


FIG. 1.—Effect of compounding ingredients on efficiency of vulcanization.—Retractive force in pounds per square inch at three times the initial length for cure giving maximum value *vs.* parts of (I) sulfur ●, (II) 2-mercaptobenzothiazole ◐, (III) zinc laurate ◑, and (IV) zinc oxide ○, per 100 parts of rubber in compounds I, II, III, and IV, respectively.

of the effects of separate ingredients, but often the reports are incomplete or not in a form suitable for ready interpretation. Therefore, experiments have been carried out to demonstrate that each of the ingredients, sulfur, accelerator, zinc oxide, and zinc soap, is necessary for efficient cross-linking.

Most rubber products produced in recent years have been based on the following general formulation, in parts by weight: 100 rubber, 1–3 sulfur, 2–50 zinc oxide, 1–5 stearic acid or zinc laurate, 0.5–1.5 2-mercaptobenzothiazole, and variable amounts of miscellaneous fillers, softeners, antioxidants, retarders, etc., depending on intended use.

Although ultra-accelerator formulations which appear to be more efficient than 2-mercaptobenzothiazole are known, such as tetramethylthiuram disulfide, their use has technical limitations for many large-volume products. Furthermore, this type of accelerator decomposes during vulcanization, in contrast to 2-mercaptobenzothiazole, substantially all of which may be recovered un-

changed[11]. Thus, the more important accelerator appeared to provide a simpler system, and the present investigation was confined to it. Other metallic oxides than zinc oxide, such as lead, cadmium, and mercury oxides, produce marked effects in vulcanization, but do not now have widespread use.

Figure 1 demonstrates the effect of variation of each of the principal ingredients while all others are held constant. In such a set of interdependent variables, the results can only be taken to show qualitatively that the vulcanizing reaction is sensitive to each. The following compounds were used (variable denoted by xx):

	I	II	III	IV
Pale crepe	100	100	...	100
Acetone-extracted pale crepe[a]	...	...	100	...
Sulfur	xx	3	3	3
Zinc oxide (Kadox)	5	5	5	xx
Zinc laurate (Laurex)	7	7	xx	7
2-Mercaptobenzothiazole (Captax)	0.5	xx	1.0	0.5

[a] Crude rubber contains appreciable quantities of fat acids; to demonstrate the effect of added zinc laurate, it is necessary to remove them, suitably by hot acetone extraction for several days.

The compounds were cured in a 0.1-inch mould for 20, 40, 60, 90, 120, 180, and 360 minutes at 141° C. The retractive force at three times the initial length, taken as the index of degree of cross-linking, was measured for each cure. The maximum value attained is plotted against the particular variable in Figure 1. The temperature of vulcanization (141° C) is in the normal range of commercial use.

It is evident that the presence of each of these four ingredients is essential to efficient cross-linking. This conclusion determined that the investigation with monoölefins should be carried out on reaction mixtures containing catalyst, zinc oxide, and soluble zinc soap in addition to sulfur. Some difficulty was caused in the isolation of the reaction products of the olefins when stearic or lauric acids or their zinc salts were used, so zinc propionate was substituted. Justification for this substitution is presented below.

The following compounds were mixed, cured, and tested under the same conditions as for the previous set, the same samples of ingredients being used:

	V	VI	VII
Master batch[a]	108.5	108.5	108.5
Zinc propionate	...	3.2	...
Zinc laurate	...	...	7

[a] 100 parts acetone-extracted pale crepe, 5 zinc oxide, 0.5 2-mercaptobenzothiazole, and 3 sulfur.

The retractive force at three times the initial length is plotted for each cure in Figure 2.

REACTION OF VULCANIZING MIXTURE WITH MONOÖLEFINS

The reaction of simple aliphatic monoölefins with the vulcanizing mixture, *i.e.*, sulfur, 2-mercaptobenzothiazole, zinc oxide, and zinc propionate, results in the formation of volatile products in which two olefin molecules are connected by one or more sulfur atoms. Nonvolatile products which contain more than two initial olefin units per molecule are also formed. The ratio of mono- to disulfides in the volatile fractions, as well as the proportion of nonvolatiles, depends on the extent of reaction and the structure of the reacting olefin. The relative yields of products are summarized in Table I.

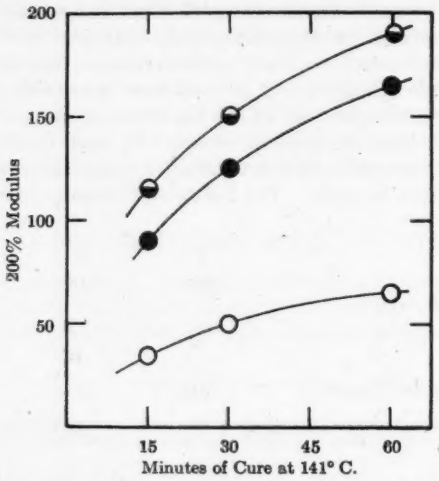
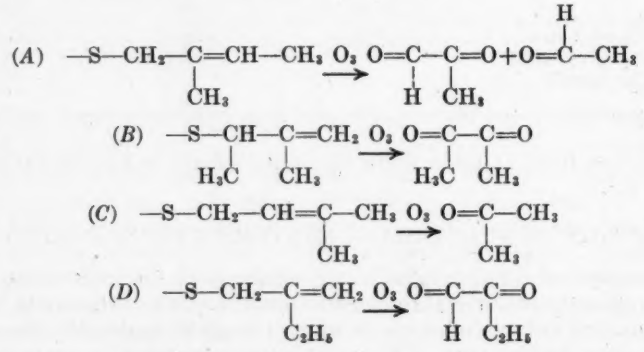


FIG. 2.—Comparison of zinc propionate with zinc laurate in effect on vulcanization. Retractive force at three times the initial length *vs.* time of cure for compounds V ○, VI ◒, and VII ●.

The volatile sulfides correspond to the simplest cross-linked structures, in which two olefin units are linked by one or two sulfur atoms connected to α-methylene groups. No products were identified which contain only one olefin unit per molecule or less than one sulfur atom with two olefin units, *i.e.*, carbon-carbon cross-linking. (Distillation of the disulfides always caused the formation of traces of thiols, due to decomposition. A five-carbon thiol was isolated from the decomposition of the disulfide of 2-methyl-2-butene. Traces of tiglic aldehyde were separated from the reaction products of 2-methyl-2-butene.)

The determination of structure of the sulfides was based on ozonolysis. The following structural formulas summarize the origin of carbonyl compounds identified from ozonolysis of methylbutene sulfides:


(A) —S—CH₂—C(CH₃)=CH—CH₃ O₃ O=C(H)—C(CH₃)=O + O=C(H)—CH₃
(B) —S—CH(H₃C)—C(CH₃)=CH₂ O₃ O=C(H₃C)—C(CH₃)=O
(C) —S—CH₂—CH=C(CH₃)—CH₃ O₃ O=C(CH₃)—CH₃
(D) —S—CH₂—C(C₂H₅)=CH₂ O₃ O=C(H)—C(C₂H₅)=O

2-Methyl-2-butene forms a mixture of mono- and disulfides which are allylic in type. The three structural units *A*, *B*, and *C* are produced in the form of isomeric symmetrical and unsymmetrical sulfides. *A* is formed in large amounts (60–70%), *C* in smaller amounts (20–30%), and *B* in smallest amounts (10%).

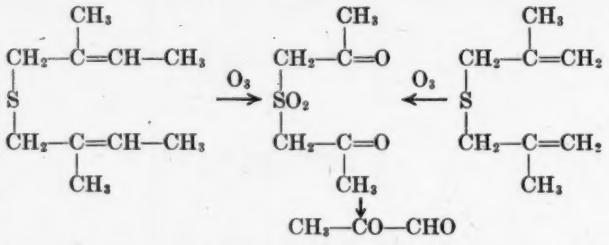
TABLE I

SUMMARY OF SULFUR-OLEFIN REACTIONS (QUANTITIES IN GRAMS)

Name of olefin	Olefin	Sulfur	Zinc oxide	Zinc propionate	2-Mercaptobenzothiazole	Temp., (°C)	Time (hrs.)	Monosulfide	Disulfide	Polysulfide	Polymer	Inorganic sulfide sulfur
2-Methyl-2-butene	325	96	160	90	13	130	7.5	24	46	10[a]	20	29
2-Methyl-2-butene	300	90	150	85	12	130	16	52	43	5[a]	25	37
2-Methyl-2-butene	234	106	0	0	0	120	21	0	0	8	4	0
2-Methyl-2-butene	234	100	0	0	0	140	23	0	31	56	105	0
2-Methyl-1-butene	240	90	150	85	12	126	12	24	32	[b]	12	[b]
2-Butene	290	90	150	85	12	130	9	10	30[c]	[b]	50	26
5-Methyl-4-nonene	200	32	0	0	0	136	6	0	0	52	2	0
5-Methyl-4-nonene	250	19	24	17	2.5	120	24	8	25	Trace	3	4
Cyclohexene	41	8	0	0	0	136	18	0	0	0	10	0

[a] Estimated. [b] Undetermined. [c] R_2S_3 plus R_2S_2.

The presence of the symmetrical monosulfide containing unit *A* was proved by ozonolysis of fraction 1*b*, Table II. The isolation of 1.4 moles of acetaldehyde per mole of sulfide indicates that part of the material must have two units *A*. The isolation of diacetonyl sulfone from the ozonolysis products is proof of the presence of the symmetrical sulfide (*bis*-β-methylcrotyl sulfide). Diacetonyl sulfone was also obtained from ozonolysis of methallyl sulfide:



By changing the conditions of formation of the dinitrophenyl hydrazone, diacetonyl sulfone forms methylglyoxal dinitrophenyl hydrazone. This formation of a carbonyl derivative from a methylene group between a sulfone and a carbonyl group serves as a valuable criterion for locating a carbon-sulfur linkage in an alkenyl sulfide. Diacetyl, resulting from product 1*a* (Table II) demonstrates the presence of α,β-dimethylallyl linkages (*B*).

Considerable amounts of acetone were formed from the ozonolysis of both fractions 1*a* and 1*b*. It is conceivable that acetone could have been formed by hydrolytic cleavage of an acetonyl sulfone. Methallyl sulfide, however, when carried through the same procedure, formed only traces of acetone. Thus it is evident that both fractions are mixtures, and the formation of acetone demonstrates the presence of γ-methylcrotyl linkages (*C*).

Fraction 1*b* thus appears to be principally the symmetrical sulfide containing unit *A*, together with a sulfide containing unit *C*. Fraction 1*a* appears to be the unsymmetrical sulfide containing units *A* and *B*, together with a sulfide containing unit *C*.

2-Methyl-1-butene forms a mixture of mono- and disulfides containing units *A* and *D*. The formation of acetaldehyde, methylglyoxal, and ethylglyoxal from ozonolysis of fraction 2*a* (Table II) demonstrates the existence of these linkages. The formation of diacetonyl sulfone from fraction 2*b*, together with 1.2 moles of acetaldehyde per mole of sulfide, demonstrates the presence of *bis*-β-methylcrotyl monosulfide. The disulfide, fraction 2*c*, contains the same structural units as the monosulfides. Presumably unit *B* is also present in small amounts in the various fractions, but it was not detected.

Since type *B* units are formed from 2-methyl-2-butene and type *A* units are formed from 2-methyl-1-butene, it is clear that an allylic rearrangement is involved. If the allylic isomers are an equilibrium mixture, unit *A* might be expected to be the principal one, by analogy with the composition of the equilibrium mixture of crotyl bromide and α-methylallyl bromide[12]. Unit *A* is the principal one formed from both 2-methyl-2-butene and 2-methyl-1-butene.

2-Butene forms crotyl monosulfide, and probably small amounts of disulfide, together with polymeric material. Ozonolysis of the monosulfide formed 1.7 moles of acetaldehyde per mole of sulfide, together with 0.5 mole of glyoxal. This is consistent with the structure $(CH_3—CH=CH—CH_2)_2S$. That glyoxal can be formed from this type of structure was proved by ozonolysis of allyl

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR OLEFIN-SULFUR REACTION PRODUCTS

Volatile sulfides	Boiling point (° C (mm.))	n_D^{20}	Percentage sulfur: Found	Percentage sulfur: Calculated	Calculated for:
1. 2-Methyl-2-butene sulfides (accelerated)					
a. α,β-Dimethallyl-β-methylcrotyl monosulfide (contains γ-methylcrotyl linkages)	60–61 (5)	1.4924–1.4929	19.3	18.8	$C_{10}H_{18}S$
b. Di(β-methylcrotyl) monosulfide (contains some γ-methylcrotyl linkages)	68 (5)	1.4982–1.4984	18.7	18.8	$C_{10}H_{18}S$
c. Disulfide (mixture of above linkages)	46–51 (0.1)	1.5292–1.5362	30.9	31.6	$C_{10}H_{18}S_2$
2. 2-Methyl-1-butene sulfides (accelerated)					
a. Monosulfide, mostly β-ethylallyl and β-methylcrotyl linkages	62–64 (5)	1.4928–1.4915	20.3	18.8	$C_{10}H_{18}S$
b. Di(β-methylcrotyl) monosulfide (contains some β-ethylallyl linkages)	66–68 (5)	1.4922–1.4945	18.7	18.8	$C_{10}H_{18}S$
c. Disulfide (mixture of above linkages)	43–50 (0.15)	1.5249–1.5321	31.1	31.6	$C_{10}H_{18}S_2$
3. Methylnonene sulfides (accelerated)					
a. Monosulfide	Molecular dist.	1.482	11.6	10.3	$C_{20}H_{38}S$
b. Disulfide		1.502–1.505	17.8–18.8	18.7	$C_{20}H_{38}S_2$
4. 2-Butene sulfides (accelerated)					
a. Dicrotyl monosulfide	62–65 (7)	1.4941–1.4921[a]	22.4	22.5	$C_8H_{14}S$
b. Disulfide + R_2S_2	50–55 (1.5)	1.5220	31.8	36.7	$C_8H_{14}S_2$
c. Trimer (R_3S_2)	62–69 (1.5)	1.5202–1.5187	28.9	27.5	$C_{12}H_{24}S_2$
5. 2-Methyl-2-butene sulfides (sulfur alone)					
a. Polysulfide	Molec. dist.	1.596–1.614	49.7–55.4	50.6	$C_{10}H_{20}S_{4.5}$
b. Disulfide (from polysulfide)	63 (0.5)	1.508–1.510[b]	31.1	31.3	$C_{10}H_{20}S_2$
6. Methylnonene sulfides (sulfur alone)					
a. Polysulfide	Molecular dist.	1.537–1.559	31.2–37.1	33.9	$C_{20}H_{40}S_{4.5}$
b. Disulfide (from polysulfide)		1.487–1.495[b]	18.7–19.0	18.6	$C_{20}H_{40}S_2$

[a] $n_D^{28.5}$. [b] n_D^{25}.

sulfide. The yield of glyoxal was comparable. The volatile material also contained a product of empirical formula R_3S_2 (where R is a C_4 unit). It contained one crotyl group (—S—CH_2—CH=CH—CH_3).

The volatile sulfides of 2-butene thus appear to be the same type as those from 2-methyl-2-butene. However, more polymeric (nonvolatile) material was formed. The proportion of nonvolatile to volatile products (weight ratio) was approximately 1:9 for 5-methyl-4-nonene, 1:3 for 2-methyl-2-butene, and 1:0.6 for 2-butene.

PROOF OF STRUCTURE OF CROSS-LINKED PRODUCTS

Olefins Used.—2-Methyl-2-butene (boiling point, 38.7° C at 766 mm.; n_D^{20}, 1.3878) was prepared by dehydration of *tert*-amyl alcohol with iodine catalyst[13]. 2-Methyl-1-butene (b.p., 31.6° C at 766 mm.; n_D^{20}, 1.3777) was separated from the above preparation of 2-methyl-2-butene by distillation through a 7-foot packed column. 2-Butene was a commercial product. 5-Methyl-4-nonene (b.p., 68.0° C at 24 mm.; n_D^{20}, 1.4288) was prepared by dehydration of dibutylmethylcarbinol (b.p., 100° C at 24 mm.; n_D^{20}, 1.4349) with anhydrous copper sulfate catalyst. The latter was prepared from *n*-butyl magnesium bromide and ethyl acetate. Cyclohexene was a commercial product.

Procedure for Sulfur-Olefin Reactions.—Reactions were carried out by heating olefin, sulfur, and other compounding ingredients at 120–140° C, with shaking or stirring. The methylnonene experiments were run under nitrogen at atmospheric pressure. The reactions of 2-methyl-2-butene, 2-methyl-1-butene, 2-butene, and cyclohexene were run in closed vessels of glass or steel. Reaction times varied between 8 and 24 hours. The olefin-sulfur reaction products were separated from the solid zinc salts by centrifuging and then washing the solids with benzene. 2-Mercaptobenzothiazole was removed by shaking the solution of olefin-sulfur products with concentrated ammonium hydroxide. In some cases unreacted sulfur and polysulfide sulfur were removed by digesting the product in an acetone-water solution of sodium sulfite. The reaction products were distilled under vacuum, the heating bath being kept below 140° C to prevent decomposition. Use of a molecular still was necessary with the methylnonene-sulfur compounds; vacuum distillation technique was used on products from other olefins (cyclohexene products were nonvolatile at 140° C and 1 mm. pressure). The compositions of the various fractions were determined by sulfur analysis and molecular weight measurements; inorganic sulfide sulfur was determined on the solids removed by centrifuging.

The proportions of starting materials, reaction time, temperature, and yields of monosulfide (R_2S), disulfide (R_2S_2), polysulfide (R_2S_x), polymer, and inorganic sulfide sulfur are summarized in Table I.

Physical Properties of Olefin-Sulfur Compounds.—The mono- and disulfide fractions of 2-methyl-2-butene, 2-methyl-1-butene, and 1-butene (catalyzed reactions) were carefully refractionated in an attempt to separate the various isomers. The monosulfides from 2-methyl-2-butene and 2-methyl-1-butene could be separated into two fractions by two careful distillations through a 44-inch spinning band column[14], although the boiling points were too close together for complete separation. The isomeric disulfides could not be separated.

Physical constants and analytical data are summarized in Table II. Numerals 1 to 4 denote total volatile fraction from the indicated olefin reacted with the entire vulcanizing mixture, as illustrated by examples in Table I.

Actually, several runs were combined for the fractionation. Numerals 5 and 6 indicate the olefins reacted with sulfur alone. Letters *a*, *b*, and *c* denote fractions of the volatile sulfides.

Ozonolysis of Products for Structure Determination.—Ozonized oxygen (about 5% ozone) was bubbled through a solution of about 0.2 gram sulfide in 100 cc. of 90% formic acid at approximately 0° C. The solution was diluted with water to 400 cc., and 100 cc. was distilled at 20 mm. to remove acetaldehyde and acetone. The distillate was neutralized with 10% sodium hydroxide, and the carbonyl compounds were removed by distillation at atmospheric pressure.

Total volatile carbonyl compounds were estimated by hydroxylamine titration[15], and acetaldehyde was estimated by fuchsin reagent[16]; acetone was determined by difference. (Ozonolysis of allyl sulfide and estimation of aldehyde by this method showed yields of less than 0.1 mole per mole sulfide, an indication that formaldehyde should not interfere in this determination, due to its low volatility at 20 mm. pressure[17].) The acetaldehyde and acetone were identified as the dinitrophenylhydrazones, prepared in 2 *N* hydrochloric acid solution[18].

Nonvolatile carbonyl compounds in the residue of the diluted, distilled solution above were reacted with hot dinitrophenylhydrazine in 2 *N* hydrochloric acid at 60–70° C, conditions which cause the formation of substituted glyoxal derivatives from the ozonolysis products of substituted allylsulfides. Glyoxal, methylglyoxal, ethylglyoxal, and diacetyl were identified from the various sulfides. The ethyl- and methylglyoxal derivatives from fractions 2*a* and 2*c* (Table II) were separated with boiling acetic anhydride. The ethylglyoxal derivative is much more soluble. The diacetyl derivative from fraction 1*a* was separated from the methylglyoxal derivative because it formed much more slowly and settled from the mother liquor. The products were recrystallized from nitrobenzene (except the ethylglyoxal derivative, which was recrystallized from acetic anhydride); and mixed melting points (decomposition) were taken with samples prepared from other sources. The methylglyoxal derivative was prepared from chloroacetone[19], the ethylglyoxal derivative from the ozonolysis products of α-ethyl-β-propylacrolein, and the diacetyl derivative was prepared from a sample of diacetyl. The glyoxal derivative was prepared from the ozonolysis products of allyl sulfide.

The nonvolatile carbonyl compounds from fractions 1*b* and 2*b*, when reacted with dinitrophenylhydrazine in 2 *N* hydrochloric acid at 5° C, formed the dinitrophenylhydrazone of diacetonyl sulfone, which was purified by successive recrystallizations from chloroform and a nitrobenzene-alcohol mixture. This

TABLE III

OZONOLYSIS PRODUCTS OF VOLATILE SULFIDE PRODUCTS

Sulfide	Products and yields (moles/mole sulfide)
1*a*	Acetaldehyde (0.7), acetone (0.5), methylglyoxal, diacetyl
1*b*	Acetaldehyde (1.4), acetone (0.5), methylglyoxal (0.6), diacetonly sulfone
1*c*	Acetaldehyde, acetone, methylglyoxal
2*a*	Acetaldehyde (0.6), ethyl- and methylglyoxals (0.6)
2*b*	Acetaldehyde (1.2), methylglyoxal (0.6), diacetonyl sulfone
2*c*	Acetaldehyde (0.8), ethylglyoxal, methylglyoxal
4*a*	Acetaldehyde (1.7), glyoxal (0.5)
4*c*	Acetaldehyde (0.8), glyoxal (0.4)
5*b*	Acetaldehyde (0.5), acetone (0.3), methylglyoxal
Methallyl	Acetone (0.1), methylglyoxal (0.7), diacetonyl sulfone (0.6)
Allyl	Glyoxal

compound was identified by synthesis from methallyl sulfide, n_D^{20} 1.4962 (prepared from methallyl chloride and sodium sulfide in aqueous alcohol), by the ozone and dinitrophenylhydrazine treatment described above.

Analysis.—Calculated for $C_{18}H_{18}O_{10}N_8S$: S, 5.9; N, 20.8. Found: S, 5.5; N, 20.4.

Table III summarizes the products isolated from ozonolysis of the various sulfide fractions. Yields, when determined quantitatively, are given in moles per mole of sulfide.

Table IV summarizes a comparison of the melting points of dinitrophenyl-

TABLE IV

COMPARISON OF DERIVATIVES WITH AUTHENTIC SAMPLES

Derivative	Table II	Melting point (° C)	Source	Melting point (° C)	Mixed melting point (° C)
Methylglyoxal	1, 2	296–7	Chloroacetone	297	297
Ethylglyoxal	2*a*, 2*c*	241–2	α-Ethyl-β-propyl-acrolein	244	242–3
Diacetyl	1*a*	312–13	Diacetyl	315	313–14
Glyoxal	4*a*	326	Allyl sulfide	327	326
Diacetonyl sulfone	1*b*, 2*b*	179–80	Methylallyl sulfide	180–81	179–81

hydrazones of nonvolatile carbonyl compounds isolated from the ozonolysis products of the indicated fractions from Table II, with authentic samples of the same derivatives made directly or by ozonolysis from the indicated source.

STATUS OF CHEMISTRY OF VULCANIZATION

Can the new information obtained in the course of this investigation, with the aid of rubber vulcanization phenomena, clarify some aspects of the mechanism of that process? Obviously, vastly more data are necessary before any complete interpretation will be possible.

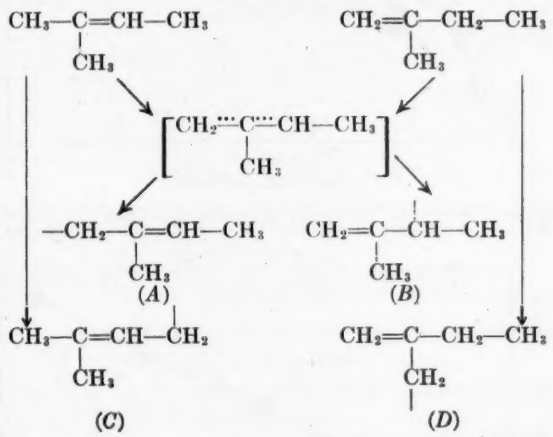
The application of this new information to the vulcanization of rubber is clearly an oversimplification of the problem; it neglects both steric or viscosity effects and cyclization reactions or other consequences of a 1,5-polyene system. It does appear reasonable to suppose that the initial steps in the reaction may be analogous. The fact that the rate of combination of sulfur with rubber is greatly increased by the presence of 2-mercaptobenzothiazole and that this catalyzed reaction is inhibited by oxygen suggests a radical-chain mechanism. The following data illustrate the inhibiting effect of oxygen on the vulcanization of compound I (Figure 1) with an initial sulfur content of 3 parts. Samples were cured in a press (absence of oxygen) for 15 minutes at 141° C. Test-pieces were placed in large glass tubes and sealed in air and *in vacuo*. After 2 weeks in an oven at 70° C, the samples were removed, analyzed, and tested with the following results:

	Retractive force[a] (lbs. per sq. in.)	Free sulfur (percentage)	Total sulfur (percentage)	Combined sulfur (percentage)
Initial	440	1.38	2.79	1.41
In air	650	1.45	2.73	1.28
In vacuo	2250	0.16	2.76	2.60

[a] At six times initial length.

The conclusion reached in the present work is that the chief products of reaction of simple aliphatic monoölefins with sulfur, zinc oxide, and soluble zinc soap in the presence of catalyst consist of the olefin bridged by sulfur at the α-methylene carbon atoms. This conclusion is consistent with a radical-chain mechanism in view of the considerable number of α-methylenic substitution reactions of the free-radical type. These were recently summarized by Farmer[20], who also suggested the probability of such a mechanism of reaction of rubber with sulfur. More recently Selker and Kemp[21], employing the methyl iodide reaction with vulcanized rubber, provided convincing evidence for the presence of allylic sulfide linkages.

The presence of type *B* groups in the 2-methyl-2-butene reaction products and the fact that type *A* groups are the chief product from 2-methyl-1-butene point to the existence of an intermediate radical or ion (resonance stabilized allylic radical represented in the formulation below), although rearrangement of the allylic sulfides subsequent to their formation is not excluded:



An allyl radical may be expected to react with free sulfur to form a free RS radical. Such radicals (perhaps of considerable stability) may interact to form di- or polysulfides possessing the structures deduced. They may also interact with catalyst to form the stable mercaptan or with the catalyst–zinc soap couple to form stable mercaptides. The tendency of a sulfhydryl radical (mercaptan in presence of peroxide) to add to an ethylenic double bond is well known[22]; it is probably responsible for other incompletely characterized products, *e.g.*, 4*c*, Table II, and nonvolatile sulfides, which are minor components of the reaction under investigation, but which apparently predominate when the olefin reacts with sulfur alone to form alkyl-alkenyl sulfides and nonvolatile material.

No mechanism of reaction of either monoölefins or rubber with the vulcanizing mixture can be satisfactory which ignores soluble zinc as a reactant. The activating effect of soluble zinc on a 2-mercaptobenzothiazole-catalyzed vulcanization is well known. Its effect is one of promoting the cross-linking process rather than sulfur combination, for which 2-mercaptobenzothiazole is effective alone in rubber. The fact that zinc sulfide is formed during vulcanization in the presence of soluble zinc has long been known, but its significance has not been appreciated. In vulcanization by mixtures under consideration here, the inorganic sulfide sulfur present in the vulcanizate is much more closely

related to the degree of cross-linking than is the combined sulfur. This is demonstrated by comparison of Figures 3 and 4, in which true combined sulfur and the inorganic sulfide sulfur, respectively, are plotted against retractive force at three times the initial length for a series of stocks and cures. ("True combined sulfur" means sulfur remaining after acetone extraction minus in-

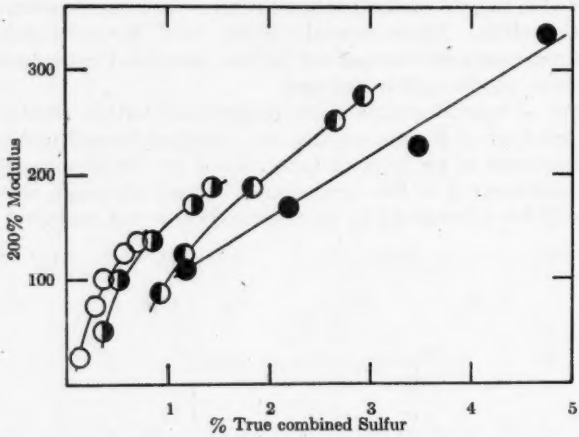


FIG. 3.—Relation of percentage "true combined" sulfur to modulus. ○ = 0.75, ◑ = 1.5, ◐ = 3, and ● = 6 parts of sulfur per 100 parts of rubber in compound 1.

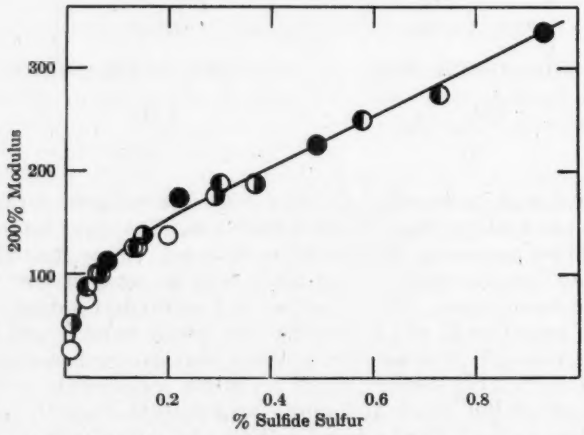


FIG. 4.—Relation of percentage zinc sulfide formed (sulfide sulfur) to modulus. ○ = 0.75, ◑ = 1.5, ◐ = 3, and ● = 6 parts of sulfur per 100 parts of rubber in compound 1.

organic sulfide sulfur; "inorganic sulfide sulfur" is calculated from the hydrogen sulfide, produced by digestion of the sample in glacial acetic acid–concentrated hydrochloric acid solution.)

Table I shows that zinc sulfide is an important product of reaction of monoolefins with the vulcanizing mixture as well. That the zinc sulfide is not formed from free hydrogen sulfide was made clear earlier. Thus it appears probable that zinc mercaptides are formed, which, in turn, react with free sulfur to

produce the disulfides as observed, or spontaneously decompose to form the monosulfides observed plus zinc sulfide. The relative importance of sulfhydryl radical to double-bond addition, compared to mercaptide formation, appears to offer a plausible explanation of the marked difference in the products of reaction of the straight-chain olefin 2-butene and of the branched-chain olefin 2-methyl-2-butene (Table I) with the vulcanizing mixture. It may also be noted that this correlates with the lower sensitivity of butadiene polymers to soluble zinc during vulcanization.

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REFERENCES

[1] Flory and Rehner, *Ann. N. Y. Acad. Sci.* **44**, Art. 4, 419 (1943); Wall, *J. Chem. Physics* **11**, 67 (1943).
[2] Garvey, Alexander, Küng and Henderson, *Ind. Eng. Chem.* **33**, 1060 (1941).
[3] Midgley, Henne and Shepard, *J. Am. Chem. Soc.* **56**, 1326 (1934).
[4] Carothers, Williams, Collins and Kirby, *J. Am. Chem. Soc.* **53**, 4303 (1931).
[5] Fisher and Schubert, *Ind. Eng. Chem.* **28**, 209 (1936).
[6] Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
[7] Jones, S. O., Thesis, Johns Hopkins Univ., **1936**.
[8] Meyer and Hohenemser, *Helv. Chim. Acta* **18**, 1061 (1935).
[9] Numajiri, *J. Soc. Chem. Ind. Japan* **40**, Suppl. binding No. 3, 111B (1937); RUBBER CHEM. TECH. **10**, 792 (1937).
[10] See, for example, "Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, Chapters VI and VIII.
[11] Smallwood and Burger, unpublished data.
[12] Young and Lane, *J. Am. Chem. Soc.* **59**, 2051 (1937).
[13] Hickinbottom, *J. Chem. Soc.* **1935**, 1280.
[14] Baker, Barkenbus and Boswell, *Ind. Eng. Chem. Anal. Ed.* **12**, 468 (1940).
[15] Platonov and Plakidina, *J. Gen. Chem.* (U.S.S.R.) **4**, 472 (1934); Houghton, *Ind. Eng. Chem. Anal. Ed.* **9**, 167 (1937).
[16] Snell and Snell, "Colorimetric Methods of Analysis", Van Nostrand Co., New York, **1937**, Vol. II, p. 61.
[17] Zimmerli, *Ind. Eng. Chem.* **32**, 1016 (1940).
[18] Iddles and Jackson, *Ind. Eng. Chem. Anal. Ed.* **6**, 454 (1934).
[19] Bulow and Seidel, *Ann.* **439**, 48 (1934).
[20] Farmer, *J. Chem. Soc.* **1942**, 513; RUBBER CHEM. TECH. **15**, 765 (1942); **16**, 467 (1943).
[21] Selker and Kemp, *Ind. Eng. Chem.* **36**, 16 (1944).
[22] Mayo and Walling, *Chem. Rev.* **27**, 387 (1940).

THERMAL EXPANSION AND SECOND-ORDER TRANSITION EFFECTS IN HIGH POLYMERS *

I. EXPERIMENTAL RESULTS *

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INTRODUCTION

Thermal expansion measurements on structural materials provide useful engineering data for design purposes and also a measure of molecular binding forces (Gruneisen's law). Both aspects of this problem are especially important in high polymers whose expansivity is some 100 times greater than for metals and glasses, and closely approximates that of liquids. High polymers exhibit, moreover, a discontinuity in thermal expansion at a characteristic temperature known as the second-order transition point. This temperature also marks a relatively abrupt change in other thermal, mechanical, electrical, and optical properties of high polymers. It is the counterpart of the critical temperature for order-disorder phenomena in alloys.

Discontinuities in the first derivative of the volume, heat content, or other primary thermodynamic functions have been termed second-order transitions by Ehrenfest[1], while Mayer and Streeter[2] have shown the relationships between different types of transitions. A considerable body of experimental data on rubber and other high polymers has been reported by a number of investigators.

Figure 1 illustrates a typical volume-temperature curve for a high polymer. It consists of two straight-line portions, connected by a curved section. Extrapolation of the straight lines yields a point of intersection corresponding to the second-order transition temperature. Below this temperature a high polymer is characterized mainly by dimensional stability and a tendency to be relatively brittle. Above this temperature creep and rubberlike properties make their appearance. The presence of cross-linking, orientation and crystallinity further complicates this simple picture. In general, however, the transition temperature is the dividing line between plastic and rubberlike properties.

This paper is concerned with determinations of the transition temperature T_m; of the cubical expansion coefficients β_1 and β_2, below and above T_m, respectively; and with the quantity $\Delta\beta = \beta_2 - \beta_1$. The relationship of these variables to each other, and their variation with type of polymer and with external experimental conditions, are interpreted by present day concepts of the structure of high polymers. The main emphasis in the actual measurements has been in exploring a wide range of temperatures in search for transition effects, with a corresponding sacrifice in accuracy.

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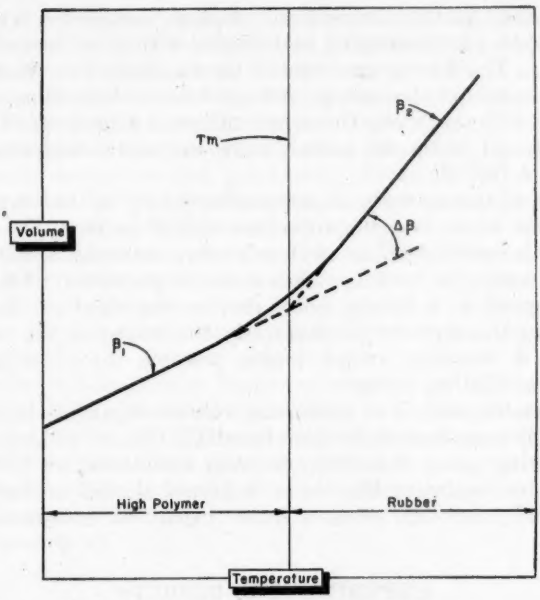

FIG. 1.—Schematic volume-temperature curve with definition of terms.

Our work is divided into three sections, of which the first, dealing with technique and experimental results, is presented here, while the two remaining sections will appear at a later date. Part II treats various theoretical aspects of the problem, and also considers some related measurements such as the brittle point. Part III will cover second-order transition effects in crystalline polymers.

EXPERIMENTAL PROCEDURE

The measurements reported here were made in two ways. Linear thermal-expansion coefficients were determined on two- to four-inch rods of the material being studied with a quartz tube dilatometer and Ames dial micrometer, according to the A.S.T.M. test D696-42T. Cubical thermal-expansion coefficients were determined by placing the sample in the bulb of a Pyrex dilatometer, surrounding it with a suitable liquid, and recording the level of the liquid in the capillary tube of the dilatometer as the temperature was varied.

Several types of dilatometers were tried, the one finally decided on being that of Bekkedahl and Wood[3]. A calibrated capillary tube, 2-mm. inside diameter, 7-mm. outside diameter, and 50 cm. long, was fastened to a cylindrical bulb of 2.22-cm. inside diameter. The sample was inserted through the open end of the bulb, followed by a hollow glass plug to prevent overheating of the specimen while the bulb was being sealed off. The dilatometer was then evacuated and filled with mercury or other liquid through the capillary tube. The height of the liquid in the capillary tube gave a measure of the volume, and was recorded as a function of temperature, either visually or automatically.

An automatic level recorder was built around a Leeds and Northrup temperature recorder. Temperature was measured with an iron-constantan

thermocouple fixed to the dilatometer. A slow, continuous temperature rise was obtained with a circulating oil bath heated with a coil receiving its current from a Variac. The Variac was coupled mechanically to a Mono-Drum unit, which slowly increased the output voltage linearly with time. The various speeds possible with the Mono-Drum unit offered a wide range of heating rates. A refrigerating coil in the oil bath extends the useful temperature range to from −30° to +180° C.

The height of the mercury in the capillary tube is determined by a stiff wire which runs down into the tube and makes contact with the mercury. When contact is established, an electronic relay activates a motor which lifts the wire until contact is broken. This motor is geared to a Selsyn generator, which is connected to a Selsyn motor driving the chart of the temperature recorder. Thus the recorder plots directly the height of the mercury *versus* temperature. A reversing switch makes possible the recording of cooling curves as well as heating curves.

The dilatometer method of measuring volume expansion has proven quite useful except for some materials which lose HCl, CO_2, or water vapor on heating. The freezing point of mercury imposes limitations on low temperature measurements, necessitating the use of isopropyl alcohol or similar liquids of high expansivity. In such cases a linear expansion measurement may be more reliable.

EXPERIMENTAL RESULTS

Table I lists the transition temperatures and cubical thermal-expansion coefficients for a number of materials.

TABLE I

SECOND-ORDER TRANSITION TEMPERATURE AND CUBICAL THERMAL EXPANSION COEFFICIENTS

Material	T_m	β below T_m	β above T_m
Polyethylene	81° C	9.4×10^{-4}	17.1×10^{-4}
Styraloy-22	82	5.4	6.7
Comm. Buna S-1	82	7.1	12.0
Comm. Buna S-2	...	5.5	...
Exptl. Buna S-3	...	5.8	...
Nylon	49	3.9	4.9

Polyethylene is a waxlike crystalline polymer which is flexible from its low temperature brittle point of −68° C to its melting point in the neighborhood of 115° C. While the low temperature end was not investigated, a pseudo second-order transition was observed at 81° C. This change in coefficient of expansion is perhaps more closely allied to the so-called premelting anomalies discussed by Van Hook and Silver[4] for the simpler lower molecular weight paraffins. The particular sample of polyethylene studied (manufactured in England) showed a melting point of 103° C in the volume-temperature curve, which was confirmed by an independent melting point determination.

Styraloy-22 presents an interesting case of a material with a fairly well defined transition temperature at 82° C, yet one which remains flexible below its transition temperature. While this plastic is more rubbery above the transition point, it nevertheless retains complete flexibility down to dry-ice temperatures, and shows no tendency to harden or embrittle. Styraloy-22 was run at different rates of heating, from two hours at each temperature con-

sidered up to as fast as 50° C per hour, without significant change in the transition temperature or expansion coefficients. However, this applied only to the case where the sample was heated slowly from equilibrium at room temperature, quite some time (12 to 24 hours) being necessary for the sample to return to its initial volume after once having been carried above its transition point.

Of the three Buna-S samples listed, the first two were prepared commercially by two different manufacturers, presumably by emulsion technique, and the third was an experimental material prepared by mass polymerization. The transition point found at 82° C for the first sample might be taken to mean that some polystyrene was present as such in the copolymer. Certain other styrene copolymers also showed a transition at 82° C, again indicating that not all of the styrene became part of a copolymer system. This method thus seems to furnish a convenient means for studying the homogeneity of copolymers.

Nylon shows a second-order transition point at 49° C, which is confirmed to some extent by the electrical measurements of Baker and Yager[5]. It is anticipated, because of the hetereogeneity of the polymer chain, that there may be other transition points. For example, a low temperature T_m characteristic of the hydrocarbon part of the chain might be expected. The volume-temperature curves were not carried above 100° C because of gas evolution (possibly water vapor).

SARAN

Saran, in contrast to the majority of thermoplastics, exists in varying degrees of crystallinity. Reinhardt[6] lists the following three modifications of saran: (1). *Crystalline.* Saran is only partially crystalline, *i.e.*, it is a mixture of crystalline and amorphous regions. (2) *Amorphous.* This state is obtained by fusing the polymer and then rapidly cooling it; this is also known as the supercooled state. (3) *Oriented.* Oriented Saran is usually produced by stretching the amorphous or slightly crystalline polymer and allowing it to crystallize further.

Both plasticized and unplasticized samples of Saran-B (vinylidene chloride-vinyl chloride) were measured with the results shown in Table II and Figure 2. It was found that T_m was independent of the amount of crystallinity for the unplasticized polymer. This agrees with results previously reported for crystalline and amorphous rubber[7]. However, in the presence of plasticizer, the T_m values decrease with increasing crystallinity. Wiley[8] has suggested that

TABLE II

TRANSITION TEMPERATURES AND CUBICAL EXPANSION COEFFICIENTS OF SARAN

Material	Crystallinity (Percentage)	T_m (° C)	$\beta_1 \times 10^4$	$\beta_2 \times 10^4$	$\Delta\beta \times 10^4$
Unplasticized Saran A[a]	75	−18.0	2.37	4.78	2.41
Unplasticized Saran B[b]	18.7	− 4.0	2.23	4.53	2.30
Same	67.0	− 4.5	0.54	1.42	0.88
Plasticized Saran B	0	− 5.5	1.18	5.71	4.53
Same	26.8	− 9.5	1.99	5.67	3.68
Same	38.6	−14.5	1.32	4.68	3.36
Same, oriented	16.5	− 7.0	1.15	4.32	3.17

[a] Saran A is pure polyvinylidene chloride.
[b] Saran B is a vinylidene chloride-vinyl chloride copolymer.

this results from increasing concentration of plasticizer in the amorphous regions to which the plasticizer is forced from the new crystalline areas. Thus the second-order transition in Saran is associated entirely with the amorphous or glassy phase. Further confirmation of this is seen in the values for $\Delta\beta$, which decrease progressively to zero as the polymer becomes more crystalline. It is interesting to note that $\Delta\beta$ for partly crystalline rubber is smaller than for completely amorphous material[8].

The various degrees of crystallinity were achieved by different heat treatments. The amount of crystallinity was estimated from the density of the

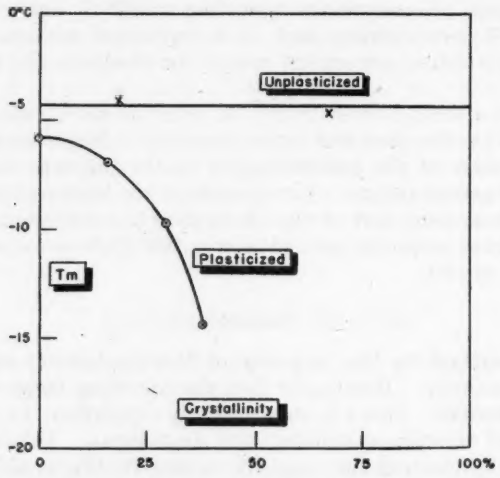

FIG. 2.—Dependence of transition temperature on percent crystallinity for plasticized and unplasticized saran B.

polymer, which method in turn had been calibrated against x-ray determinations. T_m values do depend on the Saran copolymer used, but this subject will be treated in Part III.

POLYSTYRENE

Second-order transition effects in polystyrene have been investigated very systematically by various workers[9]. Our values for T_m and for cubical expansion coefficients agree in general with previously reported values, as will be seen later in this report.

Attention might be directed here to several related transition effects found in polystyrene by widely different types of measurement. Stull[10] has observed the specific heat-temperature curve for a commercial styrene sample, as shown in Figure 3. Data were obtained with a radiation type calorimeter, using a heating rate of approximately 1° C per minute. The curve is similar to that found by Ferry and Parks for polyisobutylene,[11] as well as to that more recently published for Hycar-OR[12]. The main part of the transition occurs some 10° higher than the usually noted value of 82° C for polystyrene.

Gemant and Jackson[13], observing the logarithmic decrement of torsional vibration of a Trolitul rod, found a sharp increase at 50° C. While this is an unusually low transition temperature for polystyrene, it may result from low

molecular weight polymer or from the presence of considerable monomer. The frequency involved in this measurement was roughly 0.25 cycle per second.

A further manifestation of a second-order transition in polystyrene is contained in some data on the temperature coefficient of dielectric constant as a function of temperature, reported by Koga and Sadi[14]. The plotted curves show distinct breaks in the region from 63° C to 69° C as the frequency is varied from 5 to 10 megacycles per second. The material was Trolitul of molecular weight 60,000, vacuum-devolatilized. The general nature of their curves suggests complications from polar impurities.

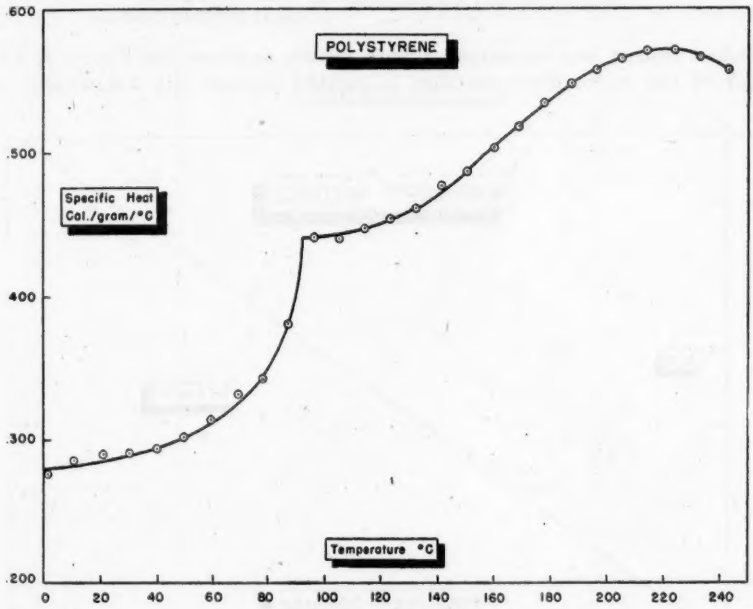

FIG. 3.—Specific heat of polystyrene.

Finally, the extensive data of Carswell, Hayes, and Nason[15] on mechanical properties of polystyrene show further aspects of a second-order transition at 82° C.

VOLUME-TEMPERATURE RELATIONSHIPS FOR TWO-COMPONENT SYSTEMS

Experiments with various copolymers as well as with mechanical mixtures of incompatible polymers having different degrees of dispersion suggested that volume-temperature studies are a convenient analytical tool for indicating homogeneity and coexistence of several phases. Several types of systems were studied: polystyrene plus a polyolefin, where the dispersion was of microscopic order; the same with dispersion of molecular order; and various copolymers. As an example of the application of thermal expansion measurements to such systems, we shall discuss the system of polystyrene plus a polyolefin where the dispersion was of microscopic order. This is one of the simplest systems studied, as there is apparently no interaction between the two components;

i.e., they exist as two separate phases. The term "microscopic dispersion" refers to the fact that electron microscope studies indicated the presence of discrete polystyrene particles around 1000 Å.U. diameter.

Polystyrene has a second-order transition point at 82° C, while the polyolefin was free from a transition point in this region. Hence, any change in the cubical expansion coefficient at 82° C must be entirely due to polystyrene, and depends on the volume of it present in the total volume. The volume fraction of polystyrene in the mixture will be given by:

$$\text{Volume fraction polystyrene} = \frac{(\Delta\beta) \text{ mixture}}{(\Delta\beta) \text{ polystyrene}}$$

Such a system was investigated with results as shown in Figure 4, where the $\Delta\beta$ of the microscopic mixture is plotted against the volume-per cent

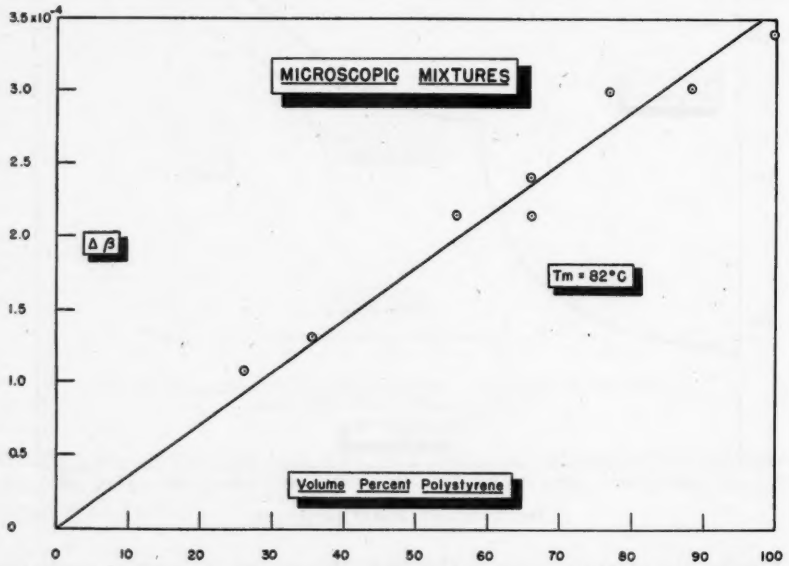

FIG. 4.—Dependence of the difference $\Delta\beta$ in cubical expansion coefficient above and below T_m on the composition of microscopic (1000A) mixtures of polystyrene and a polyolefin.

polystyrene, based on the known composition of the samples. It will be seen that a linear relationship exists between $\Delta\beta$ and volume composition. This, together with invariance of transition point with composition, is characteristic of simple, microscopic mixtures.

A similar system which has already been mentioned is that of unplasticized Saran. Here the two components are amorphous and crystalline regions, the amorphous regions being the ones producing the transition effects. In this case also we found the transition temperature to remain constant and the $\Delta\beta$ to vary linearly with percentage crystallinity. This may furnish a convenient measure for the degree of crystallinity in high polymers. This point will be treated more fully in Part III.

The system polystyrene plus a polyolefin, with dispersion of molecular order, was represented by a series of samples prepared by dissolving varying

amounts of polyisobutylene (molecular weight 12,000) in styrene monomer and thermally polymerizing the solutions. The variation of transition temperature and $\Delta\beta$ with composition is shown in Figure 5. In contrast to the microscopic mixtures, T_m is not constant with composition, but falls off abruptly after a critical composition is reached. There is also a discrepancy between $\Delta\beta$ and that which would be due to the polystyrene present. These phenomena might perhaps be ascribed to a mild plasticization of the polystyrene by the polyisobutylene, but the general behavior of this system is not that of plasticized polystyrene. Ueberreiter[16] found that the T_m composition curve for polystyrene plasticized with ethylbenzene was convex toward the composition axis, whereas our curve is concave. A similar remark holds for Jenckel and

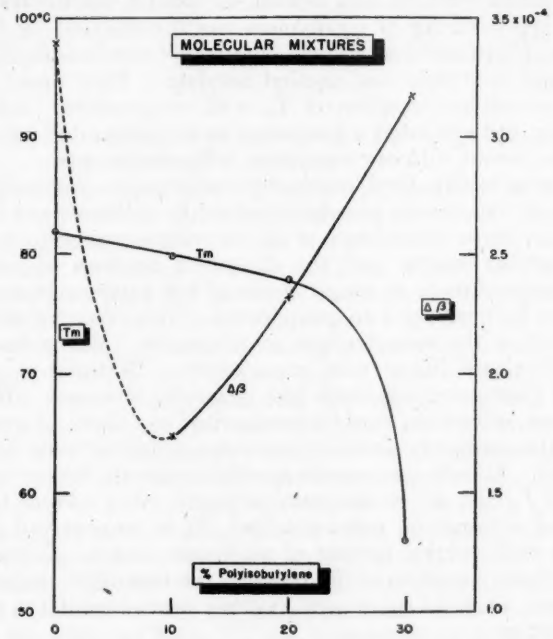

FIG. 5.—Dependence of $\Delta\beta$ and T_m on the composition of molecular mixtures of polystyrene and polyisobutylene.

Ueberreiter's data[17] on polystyrene plasticized with paraffin oil. In this latter case it was found also that $\Delta\beta$ decreased with increasing paraffin oil, whereas we found $\Delta\beta$ to increase with increasing polyisobutylene. One very interesting discrepancy is apparent in the $\Delta\beta$-composition curve. It increases almost linearly from ten per cent to thirty per cent polyisobutylene, but the extrapolation to zero per cent polyisobutylene gives a $\Delta\beta$ of 1.3×10^{-4} for polystyrene, whereas we have previously found a $\Delta\beta$ of 3.4×10^{-4} for polystyrene. The reason for this discrepancy is not clear at present. An extrapolation to one hundred per cent polyisobutylene, however, gives a $\Delta\beta$ of about 6×10^{-4}, which is in fair agreement with that found by Ferry and Parks[11]. In general, then, except for the discrepancy noted above, $\Delta\beta$ may be said to be linear with composition and its behavior similar in this respect to that of a microscopic mixture.

The assumption of a true molecular dispersion of polyisobutylene in polystyrene may not be justified for this series of samples. Polyisobutylene is precipitated from the styrene monomer as soon as any polystyrene forms. Aggregation of precipitated particles would then give rise to large, discrete particles of polyisobutylene, large enough, at least, to produce the observed scattering of light. Thus these samples likely represent a combination of microscopic and molecular dispersion of the two phases, and this may account for some of the seemingly discordant results.

Jenckel and Ueberreiter[17] have reported still another variation of this theme, that of mixtures of two polystyrene fractions of different molecular weight. The main effect here is, first, to give a T_m value intermediate between that for the two individual fractions and, second, to broaden out the transition region.

The thermal behavior of copolymers was investigated by Ueberreiter for styrene-divinyl benzene[18] and styrene-butadiene[16] copolymers, and by Jenckel[19] for copolymers of styrene and methyl acrylate. They found, in general, a continuous monotonic variation of T_m with composition. $\Delta\beta$ did not vary monotonically, but exhibited a maximum at some definite composition, which behavior is in accord with our experience with copolymers.

Summarizing briefly, then, microscopic mixtures in which there is no interaction between components are characterized by invariance of transition temperature and a linear dependence of $\Delta\beta$ on volume composition. As the particle size becomes smaller and the dispersion becomes of molecular order, transition temperature is no longer constant but varies with composition, due to interaction between the two components. This behavior will be discussed in more detail in the second paper of this series. For molecular mixtures, however, $\Delta\beta$ is still linear with composition. Mixtures of polymers with solvent type plasticizers act much like molecular mixtures. The behavior of these two types of systems may be summarized as follows: A monotonic variation of T_m with composition and a linear relationship between $\Delta\beta$ and composition are found. If both components are high polymers, the curves run between the values of T_m and $\Delta\beta$ for the pure polymers. If a solvent type plasticizer not possessing a transition point is added, T_m is lowered and $\Delta\beta$ approaches zero linearly with volume percent of plasticizer added. Copolymers show a similar monotonic variation of T_m between the transition temperatures of the pure polymers, while $\Delta\beta$ for several systems studied exhibited a maximum at some composition.

INTERNAL MELTING OF HIGH POLYMERS

The theories of fusion developed by Lennard-Jones and Devonshire[20] and independently by Harasima[21] for simple liquids predict that the product of the melting temperature in degrees (absolute) by the coefficient of volume expansion above the melting point should be a constant. Lennard-Jones and Devonshire assigned this constant a value of 0.333, while Harasima gave it a value of 0.115. This relation was found valid for a number of simple liquids; the constant would vary from one class of compounds to another but held fairly constant within a class.

Now the second-order transition temperature in high polymers has long been considered by Ueberreiter[16], Fuoss[22] and others as a kind of internal melting point. It seemed logical, therefore, to test the above-mentioned law on those high polymers for which transition temperatures and expansion coefficients are available. In Table III we find that the product transition

TABLE III

RELATION BETWEEN CUBICAL EXPANSION COEFFICIENT AND SECOND-ORDER TRANSITION POINT

Material	T_m	β above T_m	$\beta \cdot T_m$	Molar cohesion (Mark)
Polyisobutylene [23]	195° K	6.0×10^{-4}	0.117	1200
Rubber [7]	201	6.0	0.121	1300
Polyethylene	205	9.4	0.193	1000
Saran A	255	4.78	0.122	...
Supercooled Saran B	268	5.71	0.153	...
Ethocellulose [24]	316	5.05	0.160	...
Nylon (6-6)	320	4.85	0.155	5800
Methacrylate copolymer [24]	327	4.7	0.154	...
Lucite [24]	335	6.18	0.207	...
Cellulose acetate [24]	337	5.14	0.173	4800
Cellulose nitrate [24]	339	5.0	0.169	...
Polystyrene	355	5.1	0.181	4000

temperature times cubical expansion coefficient above the transition point is roughly constant within the range of 0.122 to 0.207.

It is understandable in general that such a relationship should hold because the lower the forces binding the chains together, the lower the temperature of internal melting and the easier it is for the various groups to separate from one another because of thermal energy. The last column in this table gives the intermolecular force per 5 Å.U. of chain length, as recently listed by Mark[25] for a typical series of high polymers. The general trend seems to be an increase in the transition temperature with increasing intermolecular force.

Nylon is very definitely out of line, and it appears that the high force constant listed is the one associated with the external melting temperature (285° C) of the crystalline parts of the chain; *i.e.*, with a first-order transition. The T_m value at 49° C is presumably connected with the amorphous phase just as in the case of Saran. Saran would likely have a force constant of 3000–4000 calories, which thus makes it out of order for the T_m value in Table III, but which does correspond to the melting of the crystalline phase at 190° C. These low T_m values for crystalline polymers with high intermolecular binding forces are likely possible because the chains in the amorphous regions are more or less folded up on themselves[26], so the full interchain force cannot operate.

In general the data in Table III are heterogeneous in that the various polymers may differ in molecular weight, plasticizer content, and degree of crystallinity. For example, the polyisobutylene sample with its T_m of 195° K is an extremely low molecular-weight sample. As will be shown later, increasing the molecular weight raises T_m until some limiting value is reached. Using this limiting value for T_m, the product $\beta_2 T_m$ becomes 0.123.

SUMMARY

The results presented here on second-order transitions are in general accord with what has been known for other high polymeric systems. The value of the volume-temperature technique for investigating the nature of polymeric mixtures and the homogeneity of copolymers has been emphasized. In Part II a theoretical treatment of second-order transition effects, including the related brittle point determination, will be given. Finally, Part III will permit a more expanded treatment of the behavior of Saran and other crystalline polymers.

REFERENCES

[1] Ehrenfest, Comm. Leiden, Suppl. 75b (1933).
[2] Mayer and Streeter, *J. Chem. Physics* **7**, 1019 (1939).
[3] Bekkedahl and Wood, *Ind. Eng. Chem.* **33**, 381 (1941). L. A. Wood, in a private communication, recommended the use of graduated capillaries made by Corning Glass Co.
[4] Van Hook and Silver, *J. Chem. Physics* **10**, 686 (1942).
[5] Baker and Yager, *J. Am. Chem. Soc.* **64**, 2171 (1942); Figure 5.
[6] Reinhardt, *Ind. Eng. Chem.* **35**, 422 (1943).
[7] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934).
[8] Wiley, The Dow Chemical Co., private discussion.
[9] Jenckel and Ueberreiter, *Z. physik. Chem.* **A182**, 361 (1938); Patnode and Scheiber, *J. Am. Chem. Soc.* **61**, 3449 (1939); Wiley, *Ind. Eng. Chem.* **34**, 1052 (1942).
[10] Stull, The Dow Chemical Co., unpublished data. For details on the method, see *J. Am. Chem. Soc.* **59**, 2726 (1937).
[11] Ferry and Parks, *J. Chem. Physics* **4**, 70 (1936).
[12] Bekkedahl and Scott, *J. Research Natl. Bur. Standards* **29**, 87 (1942).
[13] Gemant and Jackson, *Phil. Mag.* **23**, 960 (1937).
[14] Koga and Sadi, *Electrotech J. Japan*, Apr. **1941**, p. 79.
[15] Carswell, Hayes and Nason, *Ind. Eng. Chem.* **34**, 454 (1942).
[16] Ueberreiter, *Z. angew. Chem.* **53**, 247 (1940).
[17] Jenckel and Ueberreiter, *Z. physik. Chem.* **A182**, 361 (1938).
[18] Ueberreiter, *Z. physik. Chem.* **B45**, 361 (1940).
[19] Jenckel, *Z. physik. Chem.* **A190**, 24 (1941).
[20] Lennard-Jones and Devonshire, *Proc. Roy. Soc.* **170**, 464 (1939).
[21] Harasima, *Proc. Phys. Math. Soc. Japan* **21**, 398 (1939).
[22] Fuoss, *J. Am. Chem. Soc.* **63**, 369 (1941).
[23] Ferry and Parks, *J. Chem. Physics* **4**, 70 (1936).
[24] Wiley, *Ind. Eng. Chem.* **34**, 1052 (1942).
[25] Mark, *Ind. Eng. Chem.* **34**, 1343 (1942).
[26] Mark, "Chemistry of Large Molecules", Interscience Publishers, New York **1943**, p. 43.

STRESS-STRAIN DATA FOR VULCANIZED RUBBER UNDER VARIOUS TYPES OF DEFORMATION*

L. R. G. Treloar

INTRODUCTION

In a previous paper[1] the statistical method developed by Wall[2] for treating the problem of the elasticity of a 3-dimensional network of long-chain molecules was extended to cover the case of a homogeneous deformation of the most general type. The result was expressed by an equation representing the work of deformation per cc. of the material (W) as a function of the three principal strains, namely:

$$W = \tfrac{1}{2}G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (1)$$

where λ_1, λ_2 and λ_3 are the semi-axes of the strain ellipsoid, and G is a physical constant of the material which is related to N, the number of molecules per cc.

It is hardly necessary to emphasize the importance of this result, both in connection with the theory of large deformations of matter in general, and of rubbers in particular, and also as a means for elucidating more clearly the structure of rubber from the molecular standpoint, and the mechanism of its elasticity. The experiments described in this paper were undertaken with a two-fold purpose, first, to obtain further evidence as to the validity of the molecular-kinetic theory as an explanation of the elasticity of rubber, and secondly, to find out whether Equation (1) can usefully be employed for the calculation of the stress-strain properties of rubber in cases of practical interest.

SCOPE OF THE WORK

The types of deformation studied were: (1) 2-dimensional extension of a sheet, as in a balloon, (2) simple elongation, (3) pure shear, and (4) elongation combined with shear in a plane at right angles to the elongation. Two types of rubber were studied, one of a type which was expected to give the closest approximation to ideally elastic behavior, the other of a type more commonly used in the industry. These rubbers were compounded as follows:

8% S Rubber	Parts by weight	Latex Rubber	Parts by weight
Rubber (smoked sheet)	100	Rubber	100
Sulfur	8	Sulfur	2
Vulcanized 3 hours at 50 lbs. steam pressure (147° C)		ZnO	2.5
		Piperidine pentamethylenedithiocarbamate	1
		Vulcanized 30 min. at 100° C	

The 8% S rubber was chosen because it is of a type known to show highly reversible elastic behavior, and absence of crystallization on stretching up to 400% extension at least[3]. It has been shown by the study of the stress-tem-

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perature relations for this rubber[4] that its elasticity is determined quantitatively by the entropy effect, as required by the kinetic theory. It appeared, therefore, to be the most suitable rubber for testing the theoretical stress-strain formulas. Technically, the 8% S rubber has certain disadvantages, notably a low tensile strength, and it seemed desirable to study also a rubber having good properties from the practical standpoint, namely, a latex rubber.

The latex rubber showed very marked creep and hysteresis effects, probably due mainly to crystallization. These effects were much less noticeable at 50° C than at room temperature. For this reason the data on this rubber were all obtained at the higher temperature, the experiments being carried out in an air thermostat. The experiments on the 8% S rubber were made at a room temperature of 20 ± 1° C. In this respect the data for the two rubbers are not strictly comparable.

All the experiments on each of the rubbers were made on specimens cut from a single sheet.

2-DIMENSIONAL EXTENSION

For the production of a 2-dimensional extension, the method employed was the inflation into the form of a balloon of a circular sheet clamped round its circumference. A detailed study has been made of the state of strain over the surface of such an inflated sheet[5], and it has been found that the strain is substantially uniform over an area in the neighborhood of the centre or "pole" of the inflated sheet; in the present experiments the measurements of extension were made on two marked points lying on opposite sides of a circle of 2 mm. radius, with the pole as centre, the diameter of the unstretched sheet being 25 mm. Besides the extension, it was necessary to measure also the radius of curvature of the polar region (r), and the air pressure in the balloon (P), so that the tension T in the sheet might be obtained from the usual relation:

$$P = 2T/r \qquad (2)$$

The region of the balloon over which the shape could be considered approximately spherical covered a larger area than the region of uniform strain[5]. The measurement of r was therefore made by observation of points at a greater distance from the pole than the marked points used for the calculation of the extension ratio. This procedure gave an improvement in accuracy, particularly at low extensions.

In carrying out the experiments, air was admitted to the balloon at a convenient rate until the desired degree of distension had been reached. The air supply was then cut off while measurements of the extension, and of P and r, were made. The process was repeated at successively higher distensions. The reverse part of the curve, with decreasing distension, was obtained as the air was allowed to escape by stages. The time between successive points was not controlled, but was about four minutes.

It has often been observed with rubbers exhibiting imperfect elastic behavior that the first stress-strain curve differs noticeably from the second and later curves. For this reason the sheet was subjected to an initial distension for about two minutes at the operating temperature before measurements were begun. This introduced a slight nonrecoverable strain. The extension ratios were calculated on the basis of the new (strained) marked length, and the figure for the thickness was corrected accordingly.

If P is measured in mm. of mercury, and r in cm., the tension T in kg. per cm. of the sheet (analogous to surface tension), taking the density of mercury at 20° C to be 13.56 g./cc., is, from Equation (2):

$$T = 0.678 \text{ kg./per cm.}$$

It is convenient to refer the measurements to a sheet of initial thickness 1 cm., hence if t is the tension for such a sheet, and d_0 is the initial thickness of the actual sheet in cm.:

$$t = 0.678Pr/d_0 \text{ kg./per cm.} \quad (3)$$

per cm. of original thickness.

Compressive Force.—Since a 2-dimensional extension may be considered to be equivalent to a unidirectional compression at right angles to the plane of the sheet[1], it is possible to calculate the equivalent compressive force f from the experimental data, f representing the force on a surface of original area 1 sq. cm. The compression ratio α is obtainable from the measured linear extension ratio $1/\sqrt{\alpha}$ (assuming no volume change on extension)[6]. The tensile *stress* in the sheet is t/α, and the equivalent compressive stress is αf. Since these two are equal:

$$f = t/\alpha^2 \quad (4)$$

Table I gives the relevant experimental data, and the calculated values of f

TABLE I

TENSION IN SHEET (t) AND EQUIVALENT FORCE OF COMPRESSION FOR 8% S RUBBER AT 20° C. ORIGINAL THICKNESS 0.82 MM.

Air pressure P (mm.)	Radius of curvature r (cm.)	Linear extension ratio $1/\sqrt{\alpha}$	Compression ratio α	Tension in sheet t (kg./cm. per cm.)	Equivalent compressive force, f (kg./cm.^{2})
31	3.6_1	1.02_7	0.95	0.92	1.02
71	2.5_6	1.06_5	0.88	1.50	1.93
125	2.10	1.11_5	0.80	2.17	3.90
164	1.69	1.14	0.77	2.30	5.76
210	1.59_6	1.20	0.69	2.77	—
270	1.51_8	1.31	0.58	3.38	10.0
304	1.45_4	1.42	0.49	3.65	14.9
335	1.41_6	1.68	0.35	3.93	31.3
341	1.42_2	1.94	0.265	4.01	57.0
332	1.43	2.49	0.161	3.93	153
316	1.60	3.03	0.109	4.17	352
303	1.71	3.43	0.085	4.28	596
293	1.92	3.75	0.071	4.64	910
285	2.10	4.07	0.060	4.94	1360
280	2.28	4.26	0.055	5.27	1740
276	2.44	4.45	0.050	5.54	2180

and t, for the 8% S rubber. The experimental data for the two rubbers are represented in Figures 1 and 2, which show the tension in the sheet (t) as a function of the linear extension ratio $1/\sqrt{\alpha}$. In Figure 1, which refers to the 8% S rubber, curve (a) shows the points obtained with extensions up to the bursting point; curve (b) shows the degree of agreement between the curves obtained with increasing and with decreasing extensions. The continuous

curve in (*a*) represents the theoretical relation[1]:

$$t = G(1 - \alpha^3) \tag{5}$$

when G has the value 4.0 kg./per sq. cm. For this rubber the data are in agreement with the form predicted by the theory up to an extension ratio of 3.0; thereafter there is a progressive departure from the theoretical curve.

The latex rubber showed a much less perfectly reversible type of behavior (Figure 2 (*b*)), but the data show a similar approach to the theoretical curve up to an extension ratio of 3.0 (Figure 2 (*a*)), and a similar departure above this point. Owing to the greater strength of this rubber it was possible to continue the curve to greater extensions before bursting occurred.

(To obtain the curve (*a*), two different clamps were used, of which details are given in Reference (5). The first, an open-ended glass tube on which the

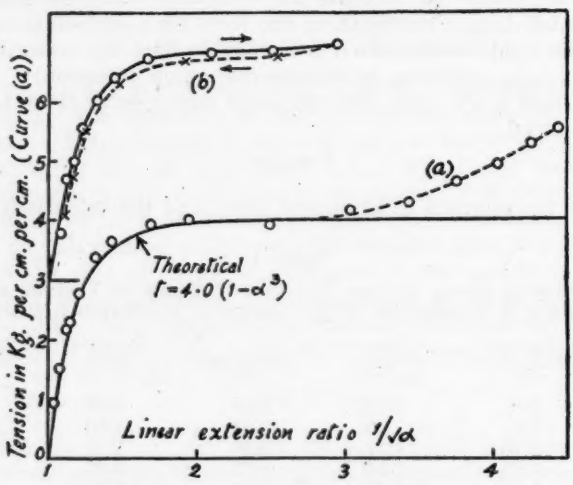

FIG. 1.—2-dimensional extension. 8% S rubber, 20° C.

rubber was bound, enabled the small distensions to be measured, but was unsatisfactory at high tensions, while the second, a metal clamp, was suitable only at higher extensions. The rubber was removed from the first clamp, and placed in the second in the middle portion of the curve. The points obtained with each clamp are separately indicated in Figure 2.)

SIMPLE ELONGATION[7]

The specimens used for the simple elongation had a width of 3 mm., a thickness of about 0.8 mm., and a marked length of 10 mm. The cross-sectional area was determined either by weighing or by measurement with a microscope and thickness gauge. The stretched lengths were measured with a travelling microscope, while weights were added to the lower clamp. The rate of extension was not controlled, but the time taken for each reading was about 1 minute. The samples were given an initial extension of about 400 per cent before readings were taken, and as in the 2-dimensional extension the

initial length and cross-sectional area were corrected for any nonrecoverable strain thus introduced.

The extension was continued until breaking occurred, but the breaking point thus determined did not represent the highest extension that might have been obtained if dumb-bell shaped specimens had been employed.

Figure 3 represents the data for the 8% S rubber. Curve (*a*) shows the complete stress-strain curve obtained with increasing extensions. Curves (*b*) and (*c*) show that the curve is reversible up to at least 450 per cent extension, but is not accurately reversible when the maximum extension is approached.

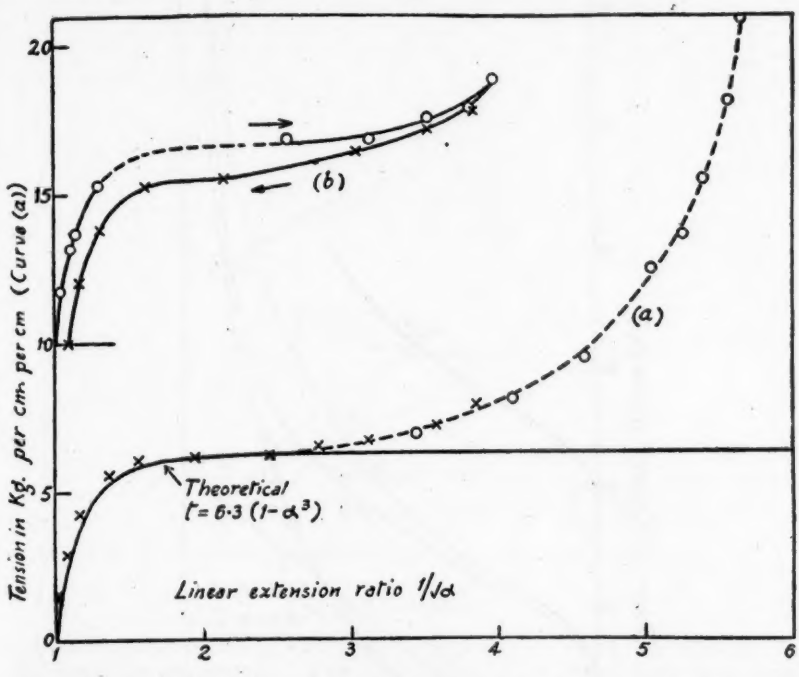

FIG. 2.—2-dimensional extension. Latex rubber, 50° C. For curve (*a*), × with glass clamp, O with metal clamp.

The theoretical form of the elongation curve is[1]:

$$f = G(\alpha - 1/\alpha^2) \tag{6}$$

If G is given the value 4.0 kg./per sq. cm. which was obtained from the 2-dimensional extension, it is seen from Figure 3 that the experimental curve begins to fall below the theoretical at about 40 per cent extension, the departure becoming greater and reaching a maximum at about 250 per cent extension, where the difference between the theoretical and experimental tension is 24 per cent. Thereafter the experimental curve turns upwards, crosses the theoretical, and finally departs from it at an increasing rate[8].

In the case of the latex rubber (Figure 4) the same general phenomena were observed, but the discrepancies between the experimental and theoretical curves were more serious. The maximum difference (excluding the high-

elongation end) was 35 per cent. The curve (*b*) shows that hysteresis was more serious than with the 8% S rubber, and it was observed in taking the readings that slow drift or "creep" effects were much more noticeable.

Compression and Elongation.—Theoretically the elongation and compression curves form a continuous curve represented by Equation (6). It is of interest to compare the experimental data on this basis. In Figure 5 the continuous

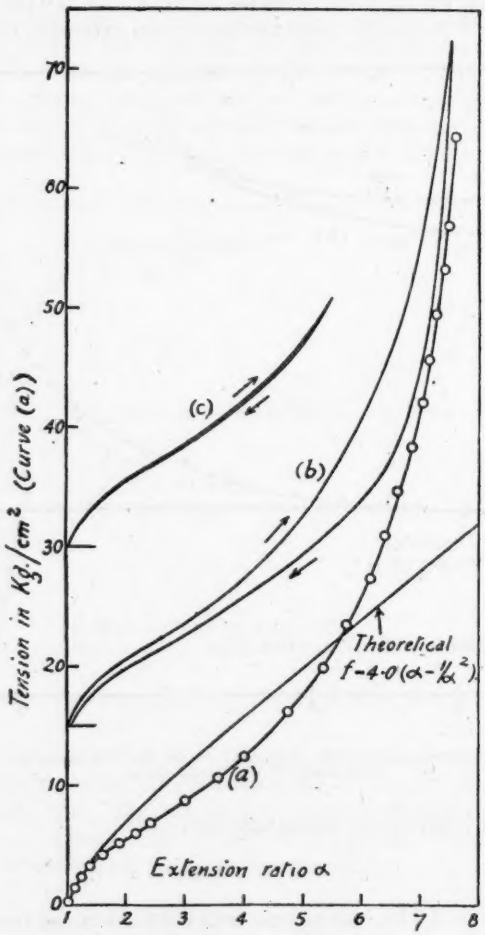

FIG. 3.—Simple elongation. 8% S rubber, 20° C.

curve represents the theoretical relation (6), with $G = 4.0$, and the experimental data for the 8% S rubber are represented by the circles. The points for $\alpha > 1$ are taken from Figure 3, while the points for $\alpha < 1$ are taken from Table I, in which the equivalent compressive force, calculated from the 2-dimensional extension data, is given. The continuity between the extension and compression branches of the curve is satisfactorily exhibited.

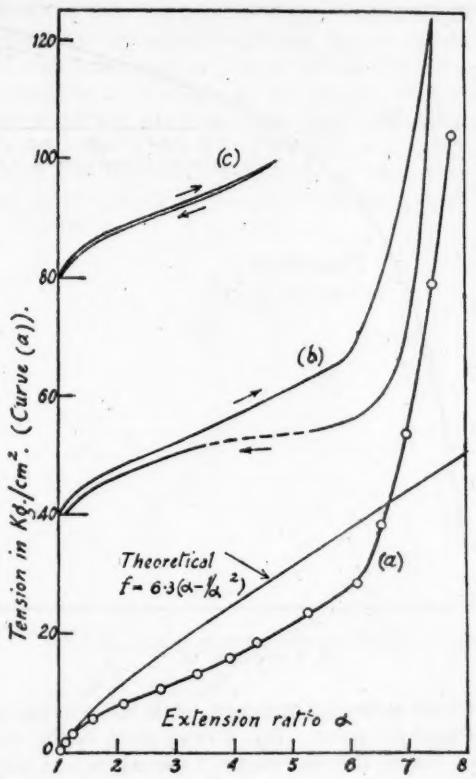

FIG. 4.—Simple elongation. Latex rubber, 50° C.

PURE SHEAR

A convenient method of applying a large shear to rubber is to stretch a short wide strip between clamps. The form of the sheet under these conditions is illustrated in Figure 6. The strip had a width of 75 mm. and an unstretched "length", between clamps, of 5 mm. It was stretched by applying weights to the lower clamp. To determine the state of strain in the stretched sheet vertical lines were marked on the unstretched sheet at distances of 7.5 mm. The position of these lines on the stretched sheet was then measured with the travelling microscope. The result is reproduced in Figure 6, in which AB and CD represent the clamped edges, and the extension ratio was 6.2.

In a pure shear, lines parallel to a given direction (in this case AB) do not change their length[1]. To a first approximation the stretched strip represented in Figure 6 is, therefore, in a state of pure shear, for with an extension of 520 per cent in the vertical direction there is a change of only 12 per cent in the horizontal direction. A more accurate approach would be obtained if the outermost segments shown in Figure 6 could be removed; this may be done, in effect, by working with two strips of different widths and subtracting the tension on the narrower from the tension on the wider strip to obtain the tension on the middle portion. This was not done in the present experiment, because

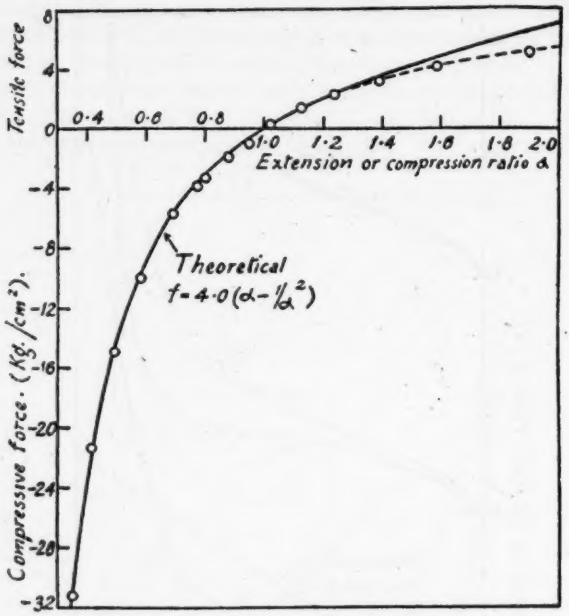

FIG. 5.—Tensile and compressive force as function of α.
8% S rubber, 20° C.

the correction was found to be insignificant, while the operation of subtraction multiplied the experimental error. But it was done in the case of combined shear and elongation, where the curvature of the edges was much greater.

It should be pointed out that the stretching of a wide strip gives a pure shear only if the volume remains unchanged.

The experimental technique employed in the stretching of the wide strip was the same as in the simple elongation. Measurements were made on marks at an original distance of 4 mm. The maximum load which could be applied was determined by slipping at the clamp or other considerations; true breaking strengths were not obtained.

From Figure 7 the tension curve for the stretching of a wide strip is seen to be very similar to the simple elongation curve. The tension is given in kg. per sq. cm. of the unstrained cross-section. The theoretical relation is:

$$f = G(\alpha - 1/\alpha^3) \qquad (7)$$

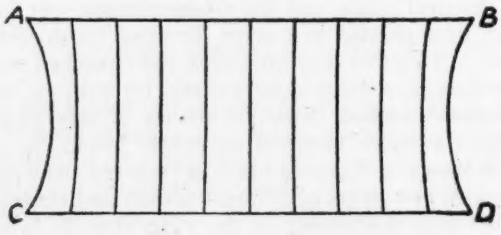

FIG. 6.—State of strain in wide sheet at $\alpha = 6.2$.

which is very similar to (6), but gives a higher initial slope, in the ratio 4:3. For the 8% S rubber the agreement with the theory (again with $G = 4.0$) is good up to 50 per cent extension; at higher extensions the experimental curve falls below the theoretical by a maximum amount of 17 per cent. The agreement is thus rather closer for the shear than for simple elongation.

Data for the latex rubber are given in Figure 8. Again the agreement with theory, when G has the value 6.3 obtained from the 2-dimensional extension, is slightly better than in simple elongation, but hysteresis effects (curve (*b*)) are considerable.

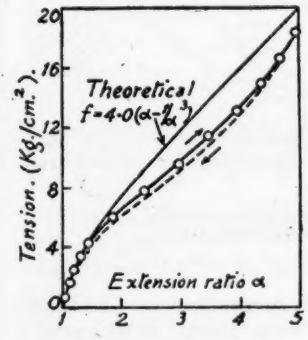

FIG. 7.—Extension of wide strip (pure shear). 8% S rubber, 20° C.

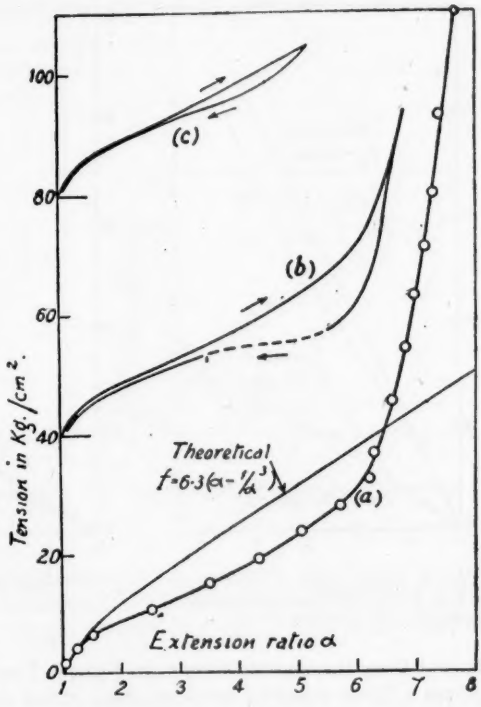

FIG. 8.—Extension of wide strip (pure shear). Latex rubber, 50° C.

The Shear Stress.—Thus far the principal tension in the direction of stretching only has been considered. The shear stress and shear strain will now be derived. The shear strain σ is given by the relation:

$$\sigma = \alpha - 1/\alpha \tag{8}$$

where α is the principal extension ratio. To find the shear stress F_σ, use is made of the work of deformation per cc., W. We have then for the tensile force f:

$$f = \mathrm{d}W/\mathrm{d}\alpha$$

and for the shear stress:

$$F_\sigma = \mathrm{d}W/\mathrm{d}\sigma$$

Hence

$$F_e = f \cdot \frac{d\alpha}{d\sigma} = f \cdot \frac{\alpha^2}{1 + \alpha^2} \tag{9}$$

from (8). Equations (8) and (9) enable the relation between shear stress and shear strain to be obtained.

The results are shown in Figures 9 (curve (*a*)) and 10. These curves were

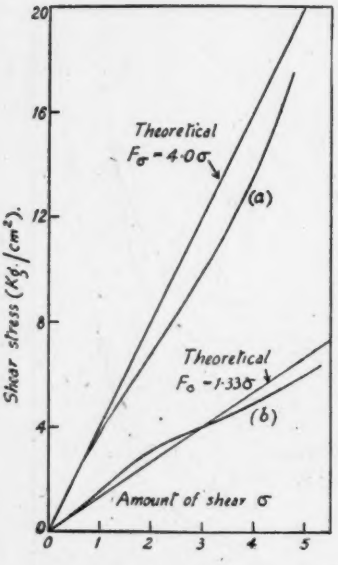

FIG. 9.—Shear stress *vs.* shear strain. (*a*) Pure shear. (*b*) Shear superposed on elongation. 8% S rubber, 20° C.

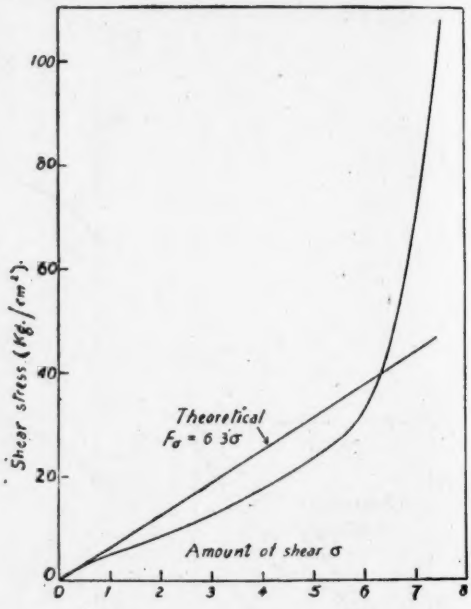

FIG. 10.—Shear stress *vs.* shear strain. Latex rubber, 50° C.

obtained from the smooth curves in Figures 7 and 8, respectively. The theory requires a linear relation between shear stress and shear strain, as indicated in the figures.

COMBINED ELONGATION AND SHEAR

The experiment described in this section was designed to test the theoretical expectation in the case of a shear applied in a plane at right angles to an initial simple elongation. The theory shows that the effective rigidity to shear should be inversely proportional to the original extension ratio[1]. The experiment involved stretching a wide strip, as described in section 5, with the difference that the rubber was stretched parallel to AB (Figure 6) before clamping.

The experiment was performed on the 8% S rubber. A strip of rubber, suitably marked, was first extended to as nearly as possible three times its original length, then clamped along its edges in clamps of width 75 mm. The edges of the clamps lay along lines originally separated by 5 mm., the distance between clamps before the application of the shear was therefore $5/\sqrt{3}$ mm.

The protruding ends of the stretched strip were then cut off along a marked line with scissors. The result was a strip of width 75 mm. extended to three times its length, which could now be sheared in a plane at right angles to the extension. For the shear measurements the microscope was focussed on marks at a distance (before shearing) of 3 mm.

Owing to the original extension there was considerable curvature at the edges of the strip, and this curvature became more serious with increasing shear. The effect was eliminated by making measurements on two strips, one having about twice the width of the other, the tension on the central uniform portion of the wider strip being obtained by difference. In Figure 11,

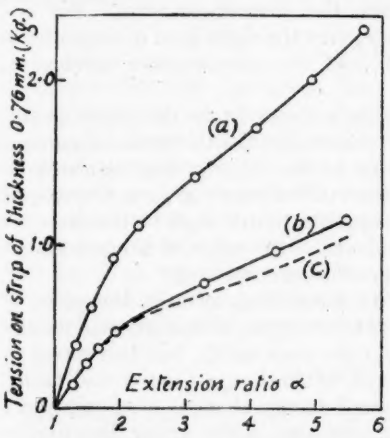

Fig. 11.—Shear superposed on elongation. (*a*) 75-mm. width. (*b*) 38.5-mm. width. (*c*) Difference. 8% S rubber, 20° C.

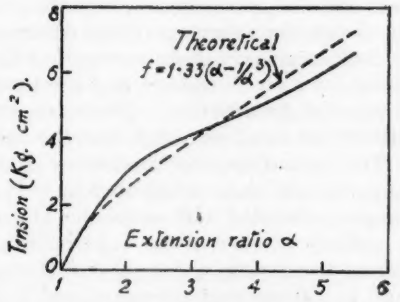

FIG. 12.—Shear superposed on elongation. 8% S rubber, 20° C.

curves (*a*) and (*b*) give the experimental data for these two strips (corrected only for a small difference in thickness), while (*c*) gives the difference. Figure 12 gives the tension in kg. per sq. cm. derived from (*c*), as well as the theoretical curve:

$$f = 1.33(\alpha - 1/\alpha^3).$$

The agreement between theory and experiment may be considered satisfactory. There is a slight inconsistency between these experimental results and the 2-dimensional extension data. For when $\alpha = 3\sqrt{3}$ (*i.e.*, 5.20) the two principal extensions are each equal to 3.0 and the tension should agree with that in the 2-dimensional extension, which, as already seen, agreed with the theoretical relation up to an extension ratio of 3.0. In the present experiment the difference amounts to about 10 per cent. If this difference were genuine it would suggest that the stresses are not independent of the way in which strains are superposed to produce a given final strain. However, the experimental errors are greatly increased by the process of subtraction of the two sets of data, and it is felt that the difference of 10 per cent is not sufficiently outside the probable error in this particular experiment to justify such a conclusion.

In Figure 9, curve (*b*) represents the shear stress-strain relationship, calculated as shown above, for the shear superimposed on an elongation of 200 per cent. The theoretical line has a slope of one-third that for the pure shear.

DISCUSSION

It has already been pointed out[1] that in the derivation of Equation (1) from the molecular network theory, it is assumed that the molecules do not approach a condition of full extension. It is this approach to full extension which is responsible for the strong upward curvature shown by the experimental curves in the three principal types of deformation when the deformation is very large. This effect will be neglected in the following discussion.

Considering the data for the 8% S rubber, the experimental curves are in general agreement with the theory. The 2-dimensional extension data agree closely with the theoretical surve, but the experimental curves for shear and elongation show significant deviations from the theoretical form. For the shear superposed on an elongation the theory gives the right kind of dependence of effective rigidity on initial elongation, and the quantitative agreement, though not exact, is satisfactory.

It would, of course, be possible to obtain a closer fit to the experimental shear and elongation data by adjusting the value of G in the theoretical formulas. The reason for referring all the deformations to the value of G obtained from the 2-dimensional extension was that this type of deformation gives the closest agreement with the theory, and the theory requires that G shall be the same for all types of deformation. Moreover, this choice of the value of G is consistent with all the data, provided that the deformations are not large.

The reason for the departures from the theoretical form in the cases of elongation and shear is not obvious. It might be suggested that internal energy changes associated with molecular alignment are responsible, but this seems to be unlikely in view of the experimental work of Anthony, Caston and Guth[9] referred to already, which showed that internal energy changes were relatively small to 350 per cent extension, and in any case were in the wrong direction to account for the present deviation. It is possible that the assumptions of the theory with regard to the distribution of molecular lengths in the stretched state, or the assumption of a single value for the molecular weight between junction points may be inadequate. It is also possible that the junction points getween molecules in the actual rubber are not as definite as the theory requires; for example, there may be effective junction points akin to entanglement-cohesions, which may break down under certain states of strain.

The statistical theory of the network is based on certain fundamental assumptions of a very general and probably far too simple character to lead to an exact correspondence with any real material. In these circumstances it is felt that the degree of agreement shown by the 8% S rubber provides a substantial confirmation of the theory as an explanation of the physical basis of rubberlike elasticity. This is particularly true for the 2-dimensional extension and the shear plus elongation, where the form of the experimental results was quite unsuspected when the theory was developed.

It is probable that Mooney's formula[10] for the work of deformation, derived on the assumption of a linear stress-strain relation in shear, might lead to a closer fit to the experimental stress-strain curve for elongation than the form (6). This application of Mooney's formula is, however, inadmissible, since the present work shows that the departure from linearity in shear is of the same order of magnitude as the discrepancy in the elongation curve.

Turning now to the latex rubber data, the agreement is less good. Evidently the structure of this rubber approximates less closely to the ideal elastic network; indeed, the elastic behavior is obviously farther from the ideal, as the

hysteresis loops show. This is probably due partly to the effects of crystallization which occurs more readily in this rubber than in the 8% S compound.

Deviations of the observed magnitude lead to the conclusion that, from the practical standpoint, the utility of the theoretical formulas is likely to be somewhat limited. This limitation arises to a considerable extent from the imperfectly definable properties of technical rubbers, and to this extent would apply to any theoretical relations that might be obtained. Nevertheless, if is felt that the theory may have value in revealing the general character of the stress-strain relations for the various types of deformation of rubber and in providing a sound, if not strictly quantitative basis for further practical development.

SUMMARY

Stress-strain data are given for two types of vulcanized rubber: (1) an 8% S rubber, and (2) a latex rubber. The types of deformation studied were simple elongation, 2-dimensional extension (or compression), pure shear, and combined elongation and shear. Comparison with the theoretical relations based on the molecular-network model shows the agreement to be good for the 2-dimensional extension, but less good for simple elongation and shear. The effect of combined elongation and shear is satisfactorily accounted for. It is concluded that the theory provides a satisfactory explanation of rubberlike elasticity, and forms a useful basis for the description of the mechanical properties of rubber subjected to large deformations of any type.

ACKNOWLEDGMENT

The author desires to express his thanks to E. Rhodes of these laboratories for the preparation of the rubber samples. The work forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943).
[2] Wall, *J. Chem. Physics* **10**, 132, 485 (1942).
[3] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935).
[4] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935); Anthony, Caston and Guth, *J. Phys. Chem.* **46**, 826 (1942).
[5] Treloar, *Trans. Inst. Rubber Ind.* **19**, 201 (1944).
[6] For the validity of this assumption, see Holt and McPherson, *Natl. Bur. Standards J. Research* **17**, 657 (1936).
[7] By "simple elongation" is meant an extension in one direction, accompanied by free contraction in directions at right angles.
[8] The author's attention has been drawn to an early paper by Baker (*Proc. Phys. Soc.* **17**, 107 (1899)), in which the approximate constancy of frequency of vibration of a stretched rubber cord over a wide range of extension is discussed. A calculation on the basis of formula (6) yields the result: $n + k\sqrt{1 - 1/\alpha^3}$, n being the frequency of vibration and k a constant. Thus n becomes substantially independent of frequency for extensions higher than about 100 per cent. Moreover, at lower extensions Baker's experimental data agree more closely with this formula than with the formula suggested by him, *i.e.*, $n = k'\sqrt{1 - 1/\alpha}$, based on the assumption of a linear stress-strain relation.
[9] Anthony, Caston and Guth, *J. Phys. Chem.* **46**, 826 (1942).
[10] Mooney, *J. Applied Physics* **11**, 582 (1940).

THE STRESS-STRAIN RELATION OF NATURAL AND SYNTHETIC RUBBERS *

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INTRODUCTION

Since the publication of the first curves showing the relation between load and elongation of vulcanized rubber, attempts have been made to fix the shape of these curves by means of algebraic formulas. Because considerable deviation from Hooke's law exists, a simple formula was not to be expected, but it seemed possible that there might be a form which would be useful in practice.

In dealing with this problem, two methods can be followed. It would be scientifically correct to start from a model of a high polymeric molecule and to calculate the stress-strain curve from this model. To make this calculation possible, however, an exact knowledge of the mechanism of the elastic deformation and of the structure of the high polymeric substance under investigation is necessary. This may be possible in the future, but up to the present this knowledge is not available. Although we have a fairly accurate idea of both the constitution and the mechanism of elongation of high polymeric substances, the exact knowledge which makes direct calculation possible is still wanting.

As long as the purely scientific method cannot be used, experimental ways remain, and many investigators have applied them. Any curve can be represented by a more or less complicated formula. The main difficulty lies in the number of constants, which must be kept as low as possible, and in the physical meaning of these constants. It was mostly a representation of the load-elongation curve that was aimed at. Hatschek[1] was the first to consider in its stead the stress-elongation curve, since this curve is much simpler.

LOAD-ELONGATION AND STRESS-ELONGATION CURVE

The load-elongation curve can be obtained by plotting the load on a test-piece against the corresponding elongation. Testing machines like the Schopper-machine give the curve automatically. As this curve gives clear information of the quality of a given kind of rubber, it is readily understood why it has become common practice to use it for this purpose. The load is calculated per unit of original cross-section.

In technical papers the term stress-strain curve is often used, which stands in most cases for the load-elongation curve, but may comprise the stress-elongation curve as well. In this paper the term "load" will be used for the ratio of the load to the original cross-section and the term "stress" or "actual stress" for the ratio of the load to the actual cross-section of the elongated test-piece.

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TABLE I

Load (σ_0) and stress (σ_w) of a pure-gum natural rubber vulcanizate

Elongation $\Delta l/l$	Load (σ_0) kg. per sq. cm. original section	Stress (σ_w) kg. per sq. cm. actual section	
0	0	0	(1)
0.5	5.5	8.3	(2)
1.0	7.3	14.6	(3)
2.0	11.5	34.5	(4)
3.0	17.3	69.2	(5)
4.0	25.0	125	(6)
4.5	32.5	179	(7)
5.0	46.2	277	(8)
5.5	69.0	448	(9)
6.0	102.5	717	(10)
6.5	143.5	1076	(11)
6.75	170	1318	(12)

Mixture: first-latex crepe 100, diphenylguanidine 0.5, mercaptobenzothiazole 0.8, sulfur 1.75, zinc oxide 5.0, stearic acid 1.0, aldol 1.0. Cure: 20 minutes 142° C. Method of testing: normal Schopper rings.

From a scientific point of view the load-elongation curve is unimportant, as it does not show what actually happens in the rubber itself. The relation between elongation and actual stress is essential, for it is only in this relation that one considers the actual forces in the stretched rubber.

As the volume of rubber remains practically constant on stretching, the actual stress can be calculated from the load and the corresponding elongation by means of the equation:

$$\sigma_w = \sigma_0 \left(l + \frac{\Delta l}{l} \right) \qquad (1)$$

where σ_w is the actual stress, σ_0 is the load (per unit of original cross-section), $\Delta l/l$ is the elongation and l is the original length of the test-piece considered. ($\Delta l/l = p/100$ where p is the elongation in per cent).

Data for load and stress of an average pure-gum mixture are given in Table I; the corresponding curves are plotted in Figure 1.

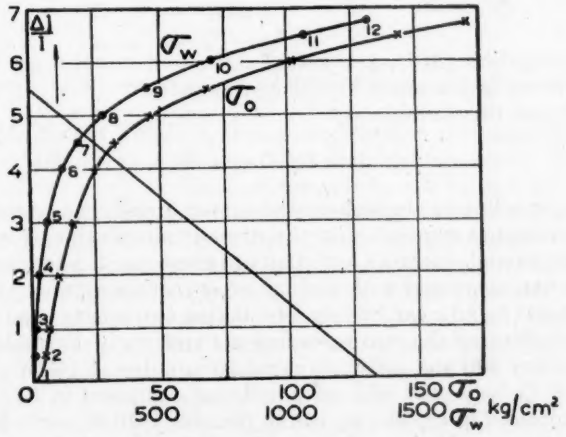

FIG. 1.—Load-elongation (σ_0) and stress-elongation (σ_w) curves of a pure-gum natural rubber vulcanizate (for its composition see Table I).

In considering Figure 1, it can be seen that a good comparison between the load-elongation and stress-elongation curve can be obtained when the scales of σ_0 and σ_w on the abscissa differ by the factor 10.

The stress-elongation curve has no inflection point, and shows an axis of symmetry which, for most pure-gum mixtures of natural and synthetic rubber, makes an angle of about 40° with the abscissa.

THE FORMULAS OF HATSCHEK AND ARIANO

Hatschek[1] has observed the resemblance between the stress-elongation curve and a hyperbola, but by considering only the first part of the curve, he came to the conclusion that it was a rectangular hyperbola, with asymptotes parallel to the stress and elongation axes. For this curve he gave the formula:

$$y = \frac{ax}{b + x} \tag{2}$$

TABLE II

Calculated and experimental load-elongation curves for a rubber 100 sulfur 8 mixture

	Load (σ_0) kg. per sq. cm. original cross-section		
		Ariano (experimental)	Author (experimental)
Elongation $\Delta l/l$	Ariano (calculated)	Cure: 40 min. 143° C flat test-pieces, 1 cm. square	Cure: 90 min. 147° C Schopper rings, 0.4 × 0.5 cross-section
0	0	0	0
0.5	2.9	2.9	5
1.0	4.6	4.6	6
2.0	6.8	6.8	7
3.0	8.8	8.8	8
4.0	10	10	9
5.0	13	13	14
6.0	17	17	23
7.0	23	23	42
8.0	33	...	77
9.0	58	...	145
10.0	235	...	...

where y = elongation ($\Delta l/l$), x = actual stress and a and b are the distances of the asymptotes to the stress and elongation axes.

Ariano[2] writes this formula as:

$$xy + bx + cy = 0 \tag{3}$$

in which form it is known throughout the rubber literature as Ariano's formula. Since it is the simplest expression for the stress-strain relation, it is often quoted as an example, though one does not attribute great significance to it, as it holds only partly when compared with various experimental curves.

The constants b and c can be found by taking two points of an experimental curve and substituting the corresponding x's and y's in Formula (3). For a mixture of rubber 100 and sulfur 8, cured 40 minutes at 143° C, Ariano gives the data -10.33 for b and 854 for c, x being expressed in kg. per sq. mm. When x is expressed in kg. per sq. cm., b remains -10.33 and c becomes 85.4.

The optimum cure however for a rubber 100 sulfur 8 mixture is 2–3 hours at 147° C, while 90 minutes at 147° C must be considered a minimum. It is

doubtful therefore, whether Ariano's test-mixture, cured only 40 minutes at 143° C, may be considered vulcanized. He measures up to a value of 1920 g. per sq. mm. for x and a corresponding value of 7.1 for y, that means a value of 23.7 kg. per sq. cm. (original section) for σ_0 and of 710 per cent for the elongation. This shows that his mixture must have been undercured, and makes it clear why no deviation between Formula (3) and the experimental curve has been observed.

That this deviation does exist, and is important when the calculated data are compared with the experimental data from a normally cured mixture, is shown by Table II and by Figure 2.

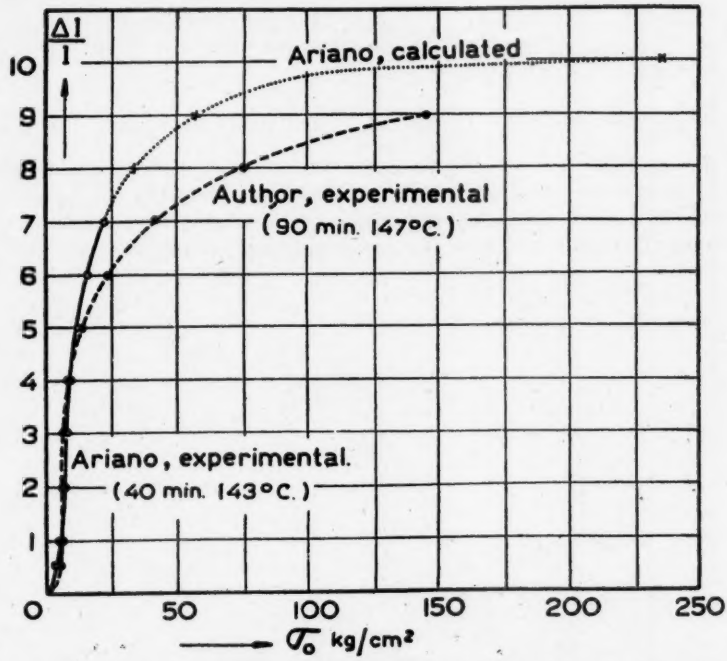

FIG. 2.—Calculated and experimental load-elongation curves for a rubber 100 sulfur 8 mixture.

From Table II and Figure 2, it can be seen that the calculated curve has far too low moduli at elongations of 700 and 800 per cent. The first part of the curve shows every evidence of undercure; the second part comes into regions which are never reached with vulcanized natural rubber. Only for the first part does agreement between calculation and experiment exist, but this cannot be taken as an experimental proof for the validity of Formula (3).

As it might be possible that by taking other values for b and c Formula (3) will hold for the author's experimental curve, sets of two points from this curve have been taken, and the corresponding data for $\Delta l/l$ and σ_w have been substituted in Formula (3). The results are given in Table III.

From Table III it can be seen that agreement does not exist, as c is not a constant at all. It is not possible to use Formula (3) for normally cured rubber; only for the first part of a curve the formula may hold more or less, but this is so in most cases.

TABLE III

Constants of Formula (3), calculated from the experimental curve for 100 rubber 8 sulfur; cure 90 minutes 147° C

Sets of points from experimental curve ($\Delta l/l$)	Calculated constants	
	b	c
3 and 6	− 7.98	53.0
3 and 9	− 9.42	68.4
1 and 6	−10.06	108.8
8 and 9	−10.17	188.7

Yet Hatschek was correct in his observation that the stress-elongation curve resembles a hyperbola. As will be shown in the following paragraphs, however, this hyperbola is not rectangular, nor does the axis of symmetry make an angle of 45° with the stress-axis.

GENERAL FORMULA FOR VULCANIZED NATURAL AND SYNTHETIC RUBBER

Observation of several stress-elongation curves of natural and synthetic rubbers, independent of the axes of coördinates to which they refer, has shown that they all possess axes of symmetry, and that from the beginning of the curves up to the breaking points the equation of a hyperbola is closely followed.

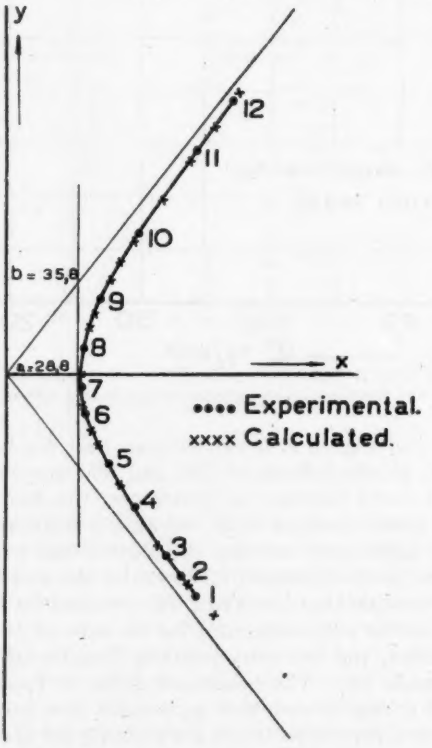

FIG. 3.—Stress-elongation curve of a pure gum natural rubber vulcanizate. (Numbering of experimental points, composition, cure and method of testing, see Table I).

In Figure 1 the axis of symmetry has been drawn. When the corresponding stress-elongation curve is turned over 39° 50′, we obtain the configuration shown in Figure 3.

In Figure 3 the axis of symmetry coincides with the abscissa; in this case the equation of the hyperbola is:

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1 \tag{4}$$

In the same way as in the case of Formula (3), Formula (4) can be checked by taking sets of two points from the experimental curve and calculating the constants a and b. The results are collected in Table IV.

TABLE IV

Constants of Formula (4), calculated from the experimental curve for a pure-gum natural rubber vulcanizate (composition and cure, see Table I)

Sets of points from experimental curve	Calculated constants		
	a	b	b/a
1 and 5	30.2	37.2	1.23
3 and 5	29.5	36.8	1.24
9 and 11	26.9	34.1	1.27
9 and 12	28.5	35.2	1.24
Mean values:	28.8	35.8	1.25

The constants remain constant, so that Formula (4) does hold. The stress-elongation curve has been calculated by using the mean values for a and b; the results are also plotted in Figure 3. They agree completely with the experimental data.

This hyperbola deviates considerably from a rectangular one; the difference is shown by the factor b/a, which is 1.25 against 1.00 for the rectangular form.

When the curve of Figure 3 is turned back into the normal position, we obtain the situation as shown in Figure 4.

The origin of the $x - y$ system happens to lie close to the ordinate of the $\sigma_w - \Delta l/l$ system, but this is not essential.

The formula for the stress-elongation curve in the $\sigma_w - \Delta l/l$ system of coördinate axes can be derived from Formula (4) in the following way:

Substitute $x = p \cos \alpha$ and $y = p \sin \alpha$. This gives:

$$\frac{p^2 \cos^2 \alpha}{a^2} - \frac{p^2 \sin^2 \alpha}{b^2} = 1 \tag{5}$$

which is the equation of a hyperbola in polar coördinates.

Now turn the $x - y$ system over an angle φ into the position of the $x_n - y_n$ system. Formula (5) becomes:

$$\frac{p^2 \cos^2 (\alpha_n + \varphi)}{a^2} - \frac{p^2 \sin^2 (\alpha_n + \varphi)}{b^2} = 1 \tag{6}$$

where α_n is the new vectorial angle of the radius vector p with the new abscissa x_n (see Figure 4).

Return to Cartesian coördinates by substituting $p \cos \alpha_n = x_n$ and

$p \sin \alpha_n = y_n$, whereby the following equation is obtained:

$$\frac{(x_n \cos \varphi - y_n \sin \varphi)^2}{a^2} - \frac{(y_n \cos \varphi + x_n \sin \varphi)^2}{b^2} = 1 \qquad (7)$$

Finally pass from the $x_n - y_n$ system to the $\sigma_w - \Delta l/l$ system by substituting $x_n = \sigma_w + p$ and $y_n = \Delta l/l + q$, where p and q are the coördinates of the

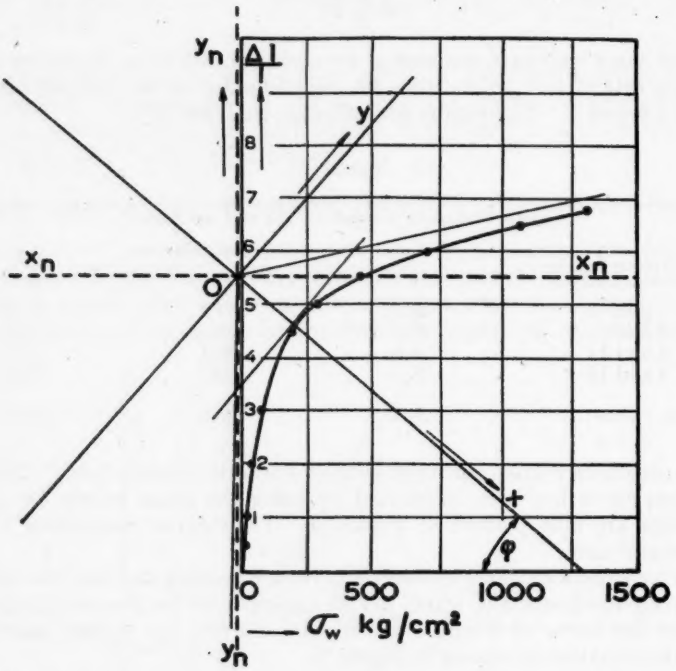

FIG. 4.—Stress-elongation curve in the three systems of coördinate axes $x - y$, $x_n - y_n$ and $\sigma_w - \Delta l/l$

origin of the $\sigma_w - \Delta l/l$ system, referred to the $x_n - y_n$ axes. Then we obtain:

$$\frac{[(\sigma_w + p) \cos \varphi - (\Delta l/l + q) \sin \varphi]^2}{a^2} - \frac{[(\sigma_w + p) \sin \varphi + (\Delta l/l + q) \cos \varphi]^2}{b^2} = 1 \qquad (8)$$

This formula holds for any hyperbola in the $\sigma_w - \Delta l/l$ system and contains the five constants a, b, φ, p and q. As the stress-elongation curve must pass through the origin of the $\sigma_w - \Delta l/l$ system, there must be a relation between these five constants. So the final formula has only four constants, and can be written:

$$\sigma_w^2 + a'(\Delta l/l)^2 + b'\sigma_w \Delta l/l + c'\sigma_w + d'\Delta l/l = 0 \qquad (9)$$

The difference from Formula (3) is contained in the first two quadratic terms and in the number of constants, which must be two more, arising from the nonrectangular shape of the hyperbola and the deviation of φ from 45°.

The constants a', b', c' and d' can be calculated from a, b, φ, p and q, but as the latter are determined graphically, it is simpler to do the same with a', b', c' and d' directly in the $\sigma_w - \Delta l/l$ system, provided that one intends to work with this system.

The practical use of Formula (9) is limited, due to the necessity of four constants and to the errors caused by the first two quadratic terms. By working with the $x - y$ system of coördinate axes, however, the very simple Formula (4) can be used.

As mentioned already, Hatschek supposed the stress-elongation curve to be a rectangular hyperbola, with the asymptotes parallel to the stress- and elongation axes. When this is the case, $a = b$ and $\varphi = 45°$, so that $\sin \varphi = \cos \varphi = \frac{1}{2}\sqrt{2}$. Substituting this in Formula (8) we obtain:

$$\sigma_w \Delta l/l + q\sigma_w + p\Delta l/l + pq + \tfrac{1}{2}a^2 = 0 \qquad (10)$$

As the curve passes through the origin, $pq + \frac{1}{2}a^2 = 0$, there remains therefore:

$$\sigma_w \Delta l/l + q\sigma_w + p\Delta l/l = 0 \qquad (11)$$

which formula is identical with Formula (3). As q and p are the coördinates

TABLE V

Composition, cure, method of testing and hyperbola constants of the rubbers investigated

	Natural rubber				Synthetic rubber	
					Neoprene	Perbunan
	Without fillers			With carbon black	Without fillers	With carbon black
Rubber (first-latex crepe)	100	100	100	...	...	...
Rubber (first-latex sheet)	...	...	...	100	...	...
Neoprene-G	...	...	...	...	100	...
Perbunan	...	...	...	...	...	100
Diphenylguanidine	...	...	0.5	0.5	...	...
Mercaptobenzothiazole	...	...	0.8	0.8	...	...
Vulkacit-AZ	...	...	...	...	...	1.8
Sulfur	8	8	1.75	2.0	...	1.5
Zinc oxide	...	...	5.0	10	5.0	15
Stearic acid	...	...	1.0	2.0	...	2.0
Blown asphalt	...	...	...	8.0	...	10
Mineral oil	...	...	...	2.0	...	...
Tricresyl phosphate	...	...	...	...	...	30
Magnesium oxide	...	...	...	...	4.0	...
Carbon black	...	...	...	44	...	57
Aldol-α-naphthylamine	...	...	1.0	1.0	...	...
Phenyl-β-naphthylamine	...	...	...	...	...	2.0
Neozone-D	...	...	...	...	2.0	...
Cure (time (minutes)	180	180	20	30	15	25
Cure (temperature (°C)	147	147	142	142	142	142
Method of testing	rings	dumb-bells	rings	rings	rings	rings
Hyperbola constants a	55.2	70.0	28.8	82.7	63.6	105.6
Hyperbola constants b	62.0	70.0	35.8	78.3	74.0	91.5
Hyperbola constants b/a	1.12	1.00	1.25	0.95	1.16	0.87
Hyperbola constants φ	39°40′	41°50′	39°50′	28°50′	41°50′	27°30′

of the origin of the $\sigma_w - \Delta l/l$ system referred to the $x_n - y_n$ axes, their absolute values also give the distances of the asymptotes to the stress- and elongation axes, which is in accordance with Hatschek (Formula (2)), while the constant a of the rectangular hyperbola is defined by:

$$a = \sqrt{-2pq} \tag{12}$$

DETERMINATION OF THE HYPERBOLA AXES OF VARIOUS NATURAL AND SYNTHETIC RUBBER MIXTURES

For each mixture (composition, cure and method of testing, see Table V) the stress-elongation curve has been carefully determined and plotted on transparent coördinate paper. Then the axis of symmetry is graphically deter-

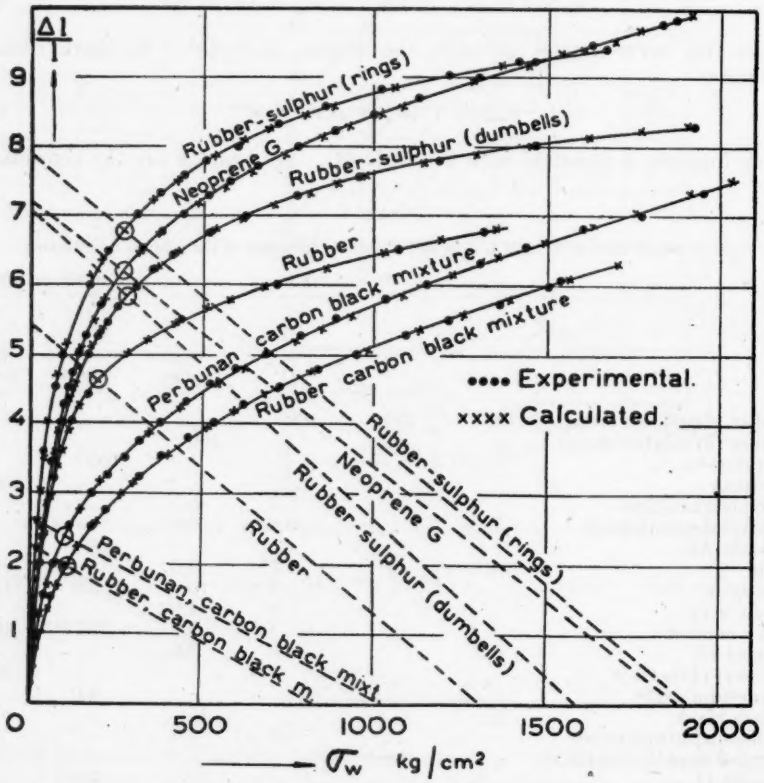

FIG. 5.—Stress-elongation curves of six rubber mixtures.

mined, so that one can pass from the $\sigma_w - \Delta l/l$ axes of coördinates to the $x - y$ system. By taking sets of two points from the experimental curve, a and b are calculated, and by repeating this process Formula (4) is checked in each case. For each mixture investigated the result was analogous to the example, given in Table IV. The mean values, determined in this way, for a, b, b/a and φ are collected in Table V.

The stress-elongation curves of these six mixtures, after graphical transformation back to the $\sigma_w - \Delta l/l$ system, are plotted in Figure 5.

As can be seen from Figure 5, complete agreement between calculated and experimental data has been reached. Formula (4) holds up to, and perhaps beyond, the point of rupture.

As far as one is warranted in drawing general conclusions from the mixtures investigated, it may be concluded that:

(1) It is possible that the stress-elongation curve is a rectangular hyperbola, but this is mostly not the case.

(2) A horizontal asymptote does not occur.

(3) No difference has been found between natural and synthetic rubbers.

(4) For mixtures without fillers, the angle between the axis of symmetry and the stress axis is about 40°; for mixtures with carbon black this angle is about 30°.

(5) The method of testing has an influence on the shape of the curve.

CONCLUSIONS

As the hyperbola is one of the simplest curves of the second order, Formulas (4) and (9) are the shortest ones available for representing the stress-elongation curve of rubber over its whole length. Trying to find further experimental formulas for this purpose will be of little use.

The value of both formulas is limited. Formula (9) has four constants, which must be determined in each separate case, as any variation as regards mixture, vulcanization and even the method of testing influences these constants. Formula (4), although very simple, is only valid in another system of coördinate axes.

Most remarkable is perhaps the fact that every stress-elongation curve has its axis of symmetry. It is not the author's intention to speculate in this paper on any physical meaning of the mathematic law which appears to govern the stress-elongation curve, but it seems probable that this symmetry is not accidental. As mentioned in the introduction, however, our present knowledge about the structure of high polymers and the mechanism of elastic deformations is not detailed enough to make precise calculations possible. A theoretical general formula for the stress-elongation curve must be in accordance with the experiments; hence it will be necessary for such a formula to show the structure of Formula (9), or Formula (4) in another system of coördinate axes. It will also be necessary to take into account the kind of material, the mixing, the vulcanization or any other stabilizing process, and even the method of testing. Such a theoretical general formula is sure to be too complicated for practical use, though of course very important from a scientific point of view. For a quick judgment of the quality of a given rubber, it is not likely that the experimental curve will lose its value.

SUMMARY

It is shown that Hatschek's formula for the stress-elongation curve of rubber—better known as Ariano's formula—does not hold for normally vulcanized rubber. The observation has been made that the stress-elongation curves of natural and synthetic rubbers follow nonrectangular hyperbolae closely and practically up to the point of rupture. The axes of symmetry of these hyperbolae make angles of about 40° with the stress-axis in the case of pure-gum

mixtures and about 30° for carbon black mixtures. A general formula has been derived which holds for all the rubbers investigated.

ACKNOWLEDGMENT

The author wishes to express his thanks to the Rubber Foundation for the permission to publish this paper.

REFERENCES

[1] Hatschek, *J. Soc. Chem. Ind.* **40**, 251 T (1921).
[2] Ariano, *India-Rubber J.* **72**, 271 (1926).

NATURAL AND SYNTHETIC RUBBER FIBERS

ELECTRON MICROSCOPE STUDIES *

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Several investigators have shown electron micrographs of various elastomers and associated fillers[1], but no systematic investigation of the structure of rubber with the electron microscope is available. Considerable attention has been given to the study of submicroscopic particles of rubber fillers, especially colloidal carbon black[2]. This work has been of great value in correlating the particle size of carbon black with the physical properties of rubber compounds, but no electron microscope evidence has been presented regarding the relation of these particles to the rubber matrix.

The object of this investigation is to obtain visual evidence of molecular configurations in rubber under varying conditions of tension, vulcanization, reënforcement, etc. Conditions must be chosen such that the density differences of regions resolvable with the electron microscope (25–50 Å.) are large enough to be observed. In thin rubber films the discontinuities of structure which may exist are apparently not readily observable. The situation is more favorable in the case of fibers, which can be prepared in a form suitable for electron microscope examination. In fibers the longitudinal tensions and freedom from lateral restraints accentuate density differences because of differential alteration of the constituent molecular chain aggregates. Accordingly, the present investigation has been concerned, for the most part, with a study of fibers from various elastomers. A number of natural and synthetic elastomers have been examined, but most of the observations are confined to Hevea rubber because of its superior properties and because it has been studied more extensively than any other elastomer.

Suitable fiber specimens can be made by spreading a thin film of rubber in an organic solvent on a water surface and allowing the solvent to evaporate. When picked up over a 200-mesh screen, the film breaks into fibers which range in width from several microns down to 100 Å. Preparation of a satisfactory fiber specimen depends on a number of conditions, such as the thickness of the spread film, size of the supporting mesh, concentration of solution, and kind of rubber. If a film is too thick, it remains unbroken across the mesh, if it is too thin, it may collapse completely. The optimum conditions must be determined experimentally for each material.

This technique is limited to some extent by the nature of the substance to be examined. It cannot be applied to rubber preparations which are completely insoluble, since a thin film can be formed only from a solution or dispersion. Some synthetic elastomers form films which do not readily break into fibers,

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and others form fibers which are too weak and plastic to support themselves across the mesh. Fiber specimens can usually be made without difficulty from the natural rubbers.

Although thin coherent films usually appear structureless in the electron microscope, they can be useful for the observation of filler particles in the rubber matrix. Rubber solutions and dispersions can also be applied directly to collodion or Formvar films for the observation of size and shape of rubber particles and filler materials.

UNVULCANIZED RUBBER

Hevea.—The first fiber specimens examined in the electron microscope were prepared from benzene solutions of pale crepe and smoked sheet (Figure 1).

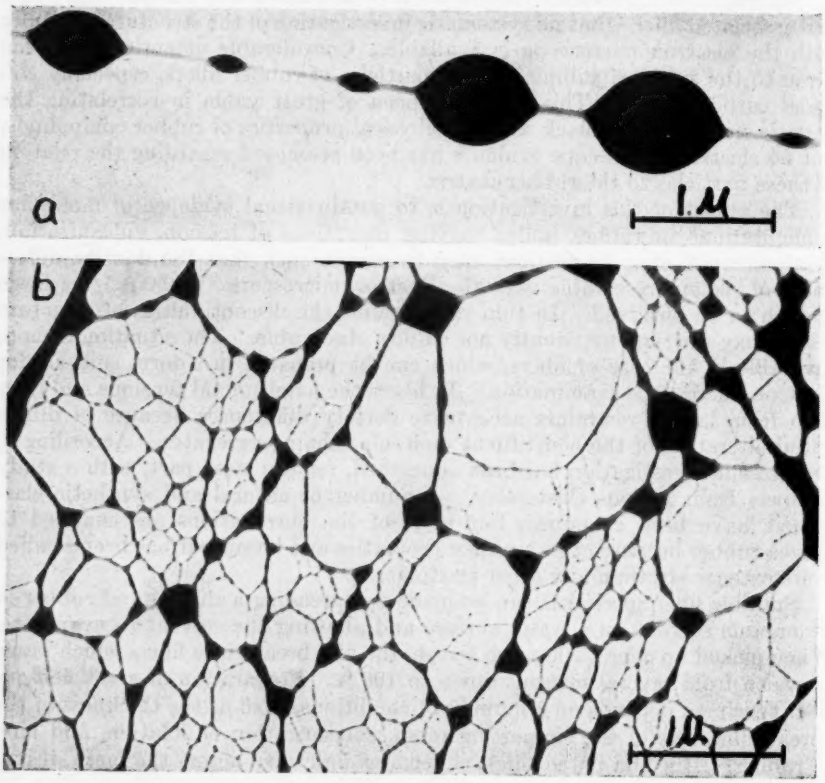

FIG. 1.—Hevea rubber fibers: (a) × 19,000, (b) × 21,000.

In any preparation many examples would be found of the two distinctive types of structures, *a* and *b*. The type shown as Figure 1*a* consists of long, slender fibers bearing numerous spherical or ellipsoidal nodules along their length. These nodules vary greatly, ranging from a few hundred Ångström units to several microns in diameter. The type shown as Figure 1*b* consists of fibrous networks, with irregularly shaped masses at the fiber junctions. The thinnest

fibers in the second type are about 100–400 Å. in width, and have a beaded appearance.

The spherical or ellipsoidal shape of the nodules in *a* is strongly suggestive of fluid regions in the fiber; the fine network structure in *b* is suggestive of considerable rigidity. Further analysis was based on the tentative hypothesis that the globular nodules and the fibrous networks are composed of relatively low- and high-molecular weight fractions, respectively. The existence of such fractions in Hevea rubber has long been known. They can be separated by virtue of their differential solubility in certain solvents[3].

Pummerer[4] termed the ether-soluble part the sol fraction and the ether-insoluble part, the gel fraction. More recently Kemp and Peters[5] and Bloomfield and Farmer[6] obtained several fractions of Hevea rubber differing in average molecular weight (measured by viscosity) by a number of fractionation procedures. The molecular weight of the dissolved portions depends on the type of solvent used and other conditions of extraction. Although the method of Pummerer gives only a rough separation, it was chosen as a convenient starting point for the electron microscope examination of rubber fractions, and the terms "sol" and "gel" will refer here to fractions obtained by this method. Sol and gel fractions were prepared from finely divided Hevea crepe by extraction with ethyl ether in a Soxhlet apparatus. The gel was dispersed in benzene, and the two components were examined separately in the electron microscope.

Films and fibers made from the sol fraction are relatively weak, and do not support themselves well across the wire mesh. Figure 2 shows that the sol fraction consists predominantly of slender fibers bearing the typical nodules. These nodules are completely absent in electron micrographs of the gel fraction. Instead, this fraction is characterized by extensive networks of extremely fine, beaded fibers with diameters down to 100 Å. and less (Figure 3). Fibers with diameters less than about 400 Å. always have a beaded appearance, as shown in Figure 4. Since thin fibers are difficult to prepare from the sol fraction because the tensions usually cause their rupture, the beaded structure is best demonstrated in the gel fraction. The distance from center to center of adjacent beads varies considerably, but most of the measured values lie between 200 and 500 Å. Experiments now in progress indicate that fibers with larger spacings occur in higher-molecular-weight fractions obtained by other fractionation procedures.

These results were considered satisfactory proof of the origin of the two types of structures in Figure 1. Thus the material shown as *a* apparently represents the sol fraction; *b* consists of a gel network with some sol portions at the fiber junctions.

When rubber fibers, prepared as described above, are exposed to the electron beam they lose elasticity, become brittle, and, on rupture, remain rigidly extended (Figure 2). This phenomenon is poorly understood at present, but it appears to involve a chemical change caused by electron bombardment.

Effect of Milling.—Samples of smoked sheet, broken down on the mill for varying lengths of time, were examined in the electron microscope by the fiber technique. The fibrous networks identified with the gel fraction of the unmilled sample became less evident in the specimens as milling time increased, until eventually the fibers were indistinguishable from those of the solfraction. Apparently the network-forming material is converted to a sol-like substance by milling. The electron microscope observations substantiate the view that mastication of rubber results in a breakdown of structure, as evidenced by an increase in plasticity of the milled material and a decrease of viscosity of solu-

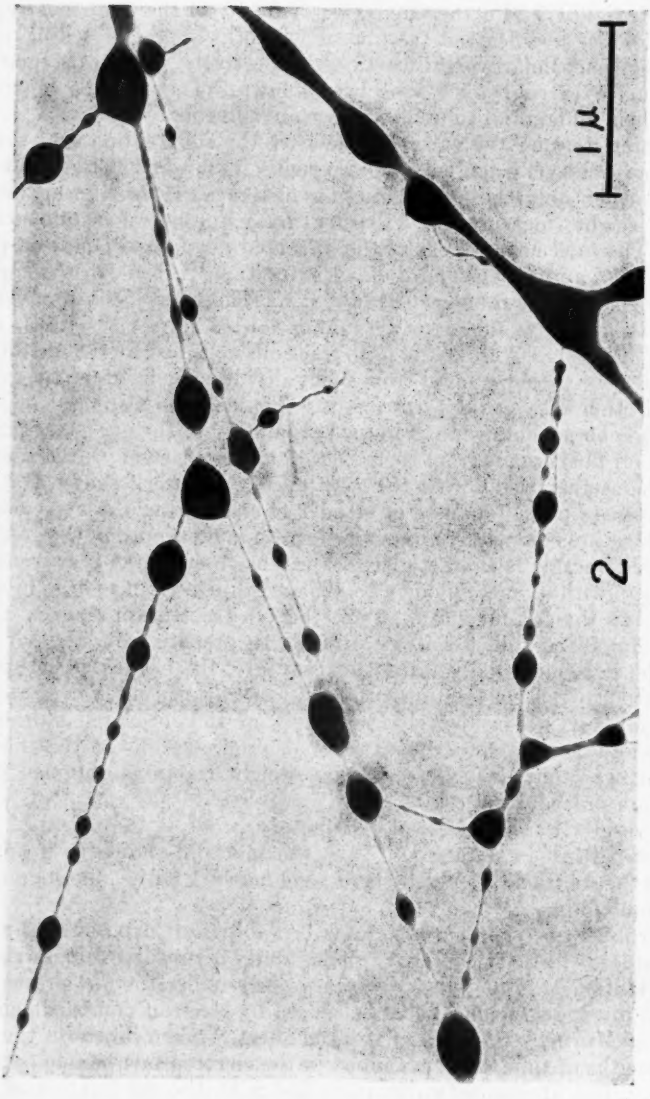

FIG. 2.—Fibers from sol fraction of Hevea rubber (×23,000).

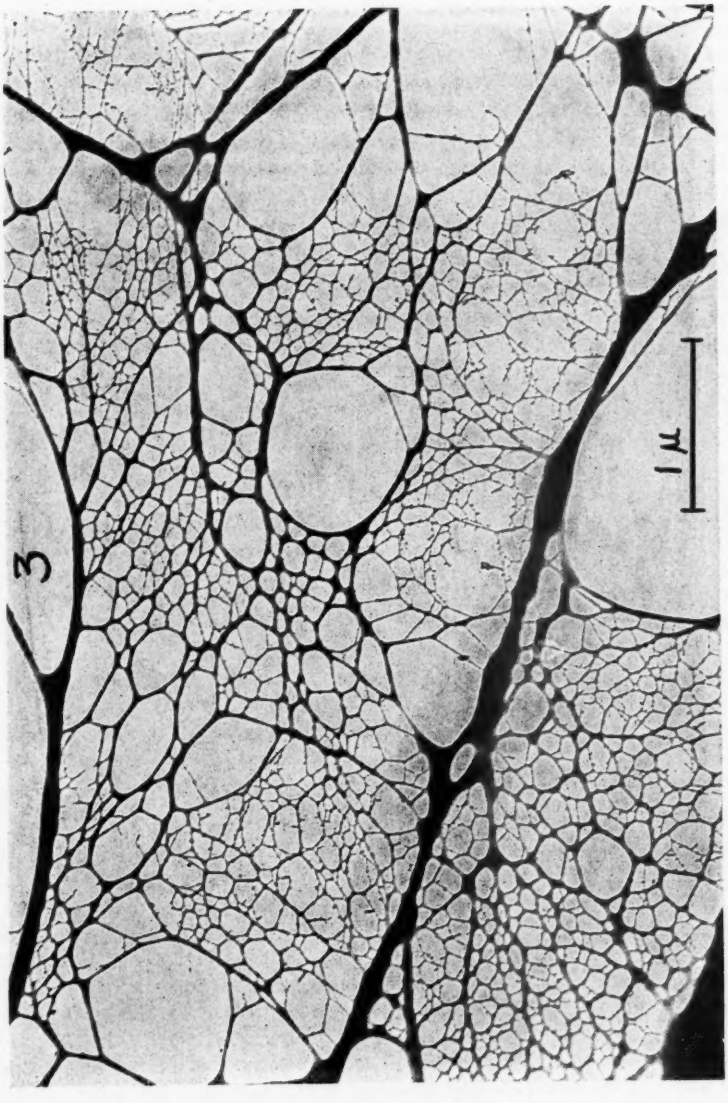

FIG. 3.—Fibers from gel fraction of Hevea rubber (× 23,000).

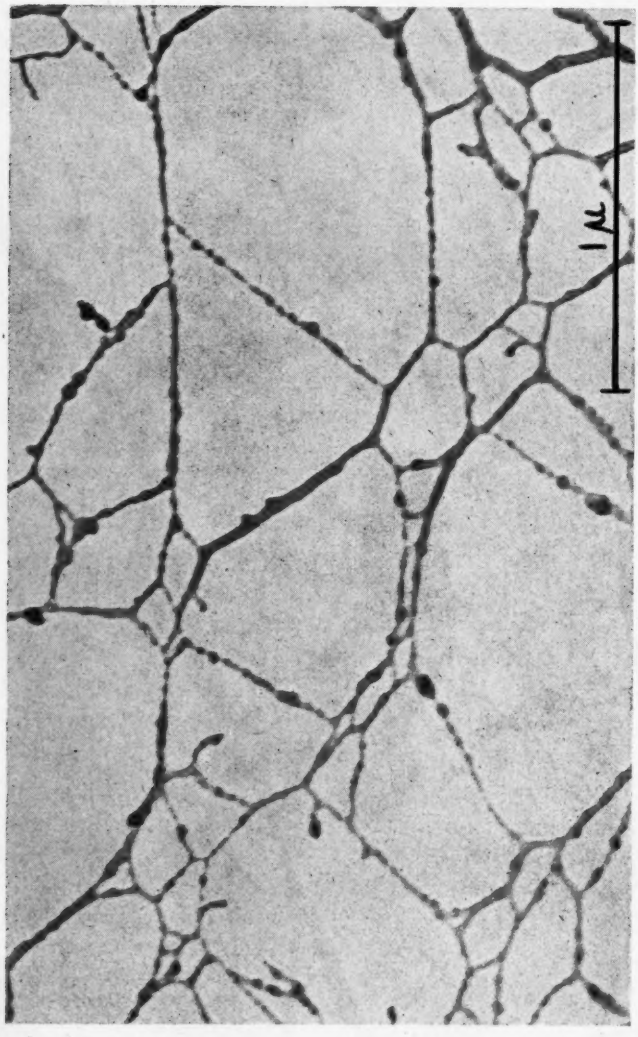

FIG. 4.—Hevea rubber fibers showing beaded structure (× 49,000).

tions. Fibers from milled rubber are weak and viscous like sol rubber, and there is some difficulty in supporting them across the specimen mesh.

Other Elastomers.—Guayule and Cryptostegia fibers show morphological characteristics similar to those of Hevea rubber. In both cases the more soluble fractions correspond in structure to the sol fraction of Hevea, the less soluble fractions correspond to the gel. The fine fibers have a beaded appearance. The structure as seen in the electron microscope reflects closely the relative amounts of the sol and gel fractions as found by other methods.

Fibers of Neoprene-GN made from benzene and carbon tetrachloride solutions vary considerably from one sample to another. The easily soluble portion produces fibers with numerous nodules resembling those from sol fractions of Hevea rubber. Sometimes the nodules are small and regularly spaced, and give the appearance of a coarse periodic structure in the fiber. In other preparations, networks of fine beaded fibers occur.

Several types of Buna-S were examined. Some were readily soluble in benzene, whereas others were dispersed in a benzene–carbon tetrachloride mixture with a Waring blendor. Films made from these materials are usually weak, and do not readily break up into small fibers. The coarse fibers have smooth contours and show no discontinuities. The few small fibers which do form are beaded and have small spherical droplets along their length, but this type of fiber is rare and cannot be taken as representative.

VULCANIZED RUBBER

The preparation of vulcanized rubber in a form suitable for electron microscope examination is complicated by the fact that well vulcanized rubber is insoluble in known solvents under conditions which do not involve serious alteration of the rubber structure. This difficulty can be avoided by vulcanizing in solution. A number of methods are available, but the most satisfactory was found to be a process of cold vulcanization originally proposed by Peachey and Skipsey[7]. This consists in reacting hydrogen sulfide and sulfur dioxide in the presence of rubber to yield an active form of sulfur which combines with the rubber. Presumably the over-all reaction proceeds according to the equation:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

For present purposes the Peachey process has the following advantages: The reaction proceeds rapidly at room temperature and is reasonably quantitative. Complications due to accelerators, activators, and reaction products are avoided. The sulfur is produced in a highly disperse form which ensures homogeneity of the sample. Finally, a wide range of degree of vulcanization can be produced at will.

An apparatus was constructed so that hydrogen sulfide and sulfur dioxide, in the ratio of 2:1, could be introduced simultaneously into rubber solutions from separate, calibrated burets. The total amount of sulfur formed in the reaction depended on factors such as time, temperature, concentration of solution, etc., but was reasonably constant under specific conditions.

For calibration, measured amounts of the gases were introduced into rubber solutions and allowed to react for definite times. The solvent and uncombined gases were driven off, and the rubber was analyzed for free and combined sulfur by standard procedures[8]. A series of calibration curves was obtained which gave the amounts of total and combined sulfur as a function of the volume of reacting gases for specified conditions.

FIG. 5.—Fibrous network obtained from milled Hevea rubber vulcanized in solution (× 23,000).

Rubber solutions vulcanized by the Peachey process may form gels which render the preparations unsuitable for electron microscope examination. Formation of insoluble gels depends on the amount of combined sulfur, concentration of solution, and other factors. Benzene solutions of freshly milled Hevea rubber of 0.25–0.4 per cent concentration did not gel within 24 hours or longer over a wide range in amount of combined sulfur.

Hevea smoked sheet milled for about 9 minutes was vulcanized in a 0.4–0.5 per cent benzene solution with varying proportions of sulfur and examined in the electron microscope. The unvulcanized material produced the usual weak fibers of milled rubber with many fluid droplets along their length and at fiber junctions. This material displays a structure similar to that of sol rubber, as shown in Figure 2. Only a small amount of combined sulfur (around 0.2–0.3 per cent) is required to strengthen the material substantially and produce a striking effect on the structure as observed in the electron microscope. The milled material is converted into a highly branched fibrous network, with some "fluid" regions remaining at the fiber junctions. Higher sulfur combinations produced stronger, more extensive networks, with practically no fluid regions at the fiber junctions, as shown in Figure 5, which is in marked contrast to the unvulcanized material typified by Figure 2. Many of the fibers in the networks have diameters less than 100 Å.; those below about 400 Å. have a beaded appearance. The distance between adjacent beads in this type of preparation varies from about 200 to 500 Å. These fibrous networks are essentially indistinguishable in the electron microscope from those of gel rubber.

Fibrous networks produced from solutions vulcanized beyond about 1.0 per cent combined sulfur differ from those with lower combined sulfur in that extensive networks of coarse fibers (500–900 Å. in diameter) appear (Figure 6) which have a well defined periodic variation in density along their length (Figure 7). These fibers always appear over an appreciable fraction of the total specimen area. They apparently represent some structural modification related to the increased sulfur content. The length of the periodic density variation ranges from 400 to 1000 Å.

If the proportion of combined sulfur is increased, the films spread on water lose strength and become extremely brittle. Such films (200–400 Å. thick) can be shattered by mechanical agitation with a needle. This material manifests no obvious fibrous structure when viewed in the electron microscope.

Buna-S samples were also vulcanized by the same method, although the efficiency of the reaction, as indicated by the proportion of sulfur formed and the proportion combined, differs from the values found for natural rubber. Vulcanization results in an increased toughness in spread Buna films and a tendency to form fibrous networks.

CARBON BLACK IN RUBBER

The use of colloidal carbon black as a filler to modify the physical properties of rubber is one of the most important aspects of rubber technology. Since the particle sizes of most colloidal carbons are within the resolution of the electron microscope, direct observation of the filler particles in rubber may contribute to an understanding of reënforcing action.

Electron micrographs of commercial carbon blacks before they are milled into rubber show that the particles occur in large clumps. During the milling operation the clumps are broken down to some extent and dispersed. Freshly milled samples of carbon black in rubber, dissolved in benzene and applied to

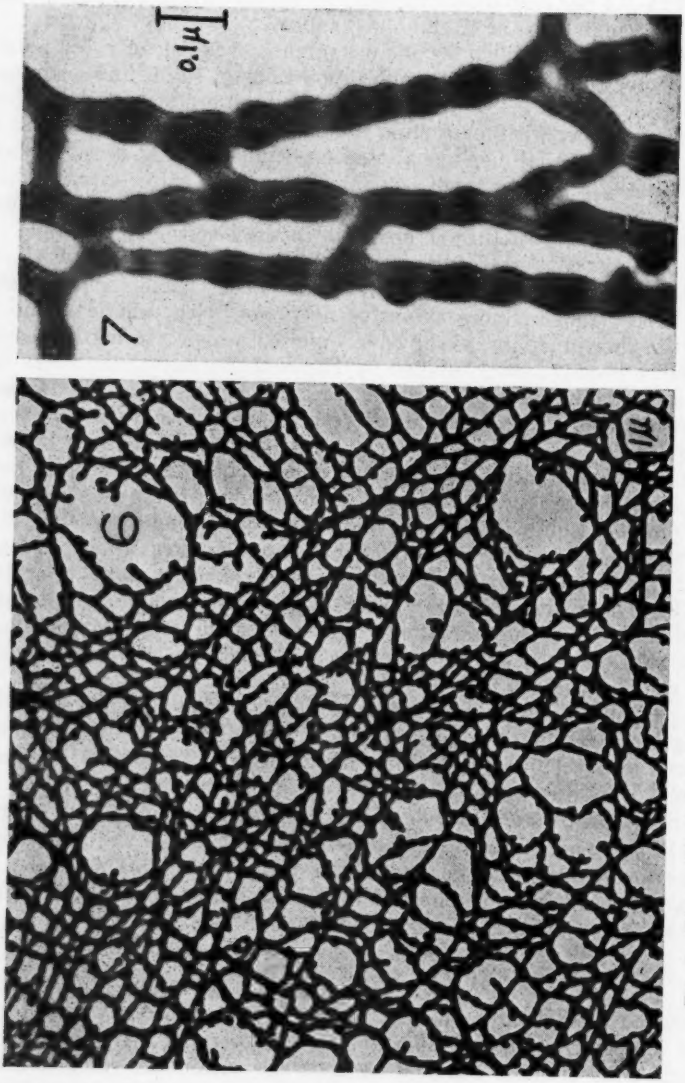

FIG. 6.—Fibers with relatively high combined sulfur obtained by cold vulcanization of Hevea rubber (×24,000).
FIG. 7.—Fibers with relatively high combined sulfur obtained by cold vulcanization of Hevea rubber, highly magnified to show periodic structure (×94,000).

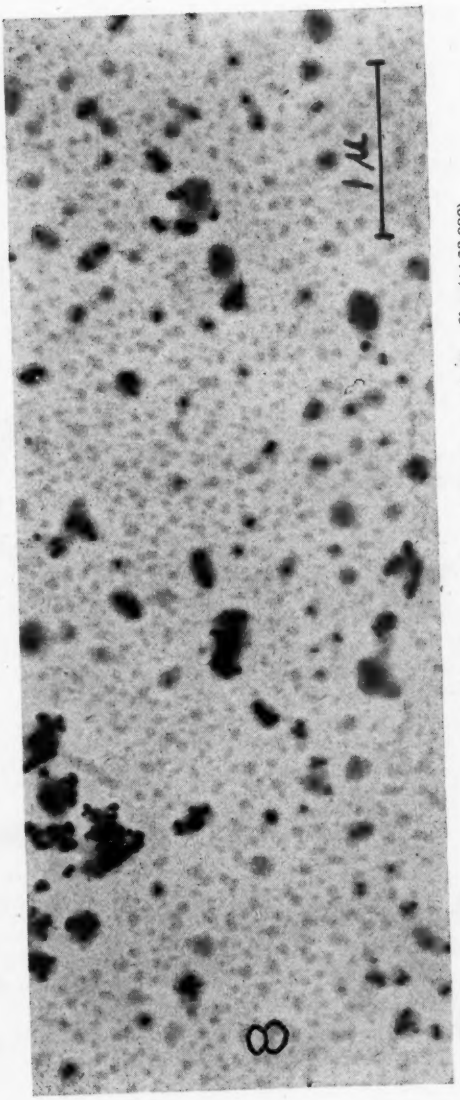

FIG. 8.—Carbon black in the rubber particles, deposited on collodion film (× 23,000).

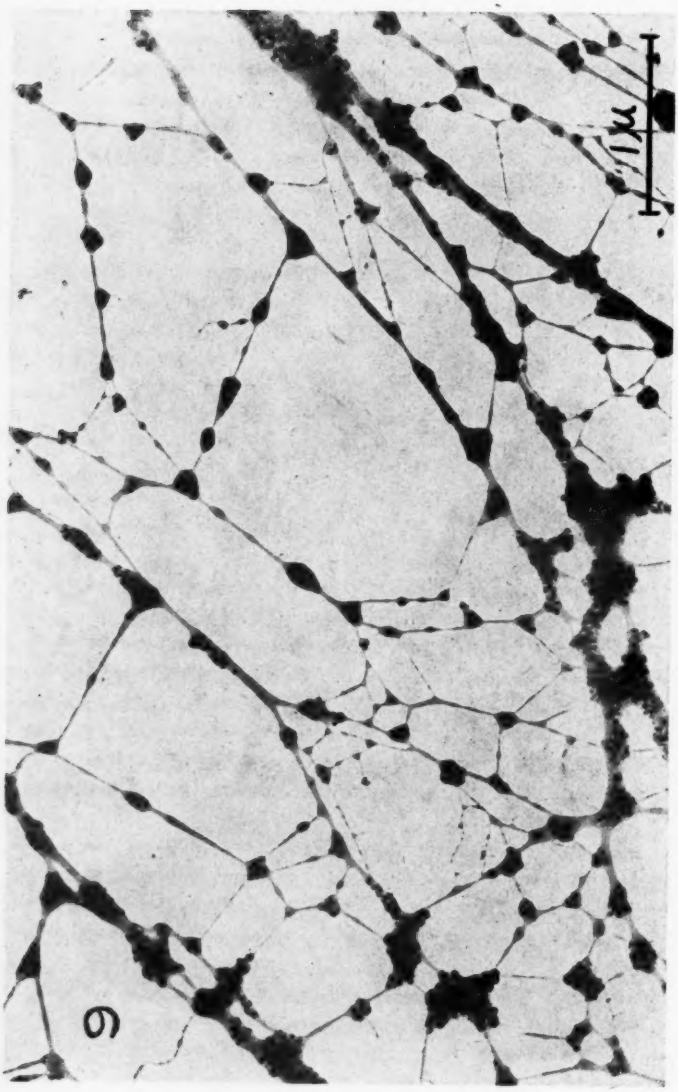

FIG. 9.—Gel-like fraction of recovered Hevea rubber which contains channel black (×24,000).

collodion films, show small discrete rubber particles with carbon black embedded in them (Figure 8). The carbon particles appear singly and in groups, and are always surrounded by a thin layer of rubber. Similar results were obtained for a wide variety of carbon blacks, including reënforcing, semireënforcing, and nonreënforcing types. If the carbon black is added to a rubber solution and dispersed mechanically instead of being milled in, the carbon particles remain in relatively large aggregates and do not become incorporated in the dissolved rubber particles.

Fiber preparations of freshly milled carbon black rubber compounds show the structure typical of milled or sol rubber preparations. The carbon black tends to accumulate in the nodules, coarse fibers, and film regions.

Rubber compounds containing channel black, which have been allowed to recover for a few weeks or so after milling, are only partly soluble in benzene. When the benzene-soluble fraction is extracted, a gel-like mass remains, which contains most of the black. This portion can be dispersed in benzene by mechanical means, and fibrous networks obtained from the dispersion are similar in many ways to those obtained from the gel fraction of pale crepe. The carbon black appears throughout the coarse fibers and in nodules or clumps in the finer fibers. Many fibers have diameters less than the average of channel black particles (Figure 9).

Freshly milled carbon black-rubber compounds were dissolved in benzene and vulcanized by the Peachey process. Fiber specimens show the usual networks associated with vulcanized rubber (Figure 10). Most of the carbon black is located in the coarse fibers and film portions.

In all these preparations there is a tendency for the carbon particles to aggregate into clumps and chains. Such an effect would decrease the surface area of the carbon available to the rubber, and may be an important consideration in correlating reënforcement phenomena with surface area measurements. There appears to be no regularity in the location of carbon particles in rubber fibers. Regions containing a high concentration of carbon black do not readily break apart into fibers, and there is no apparent tendency for fibers under tension to break at points containing carbon. Apparently there is a relatively strong adhesion of rubber to carbon surfaces, but the electron microscope at present can give no information as to magnitude or nature of forces involved.

DISCUSSION OF RESULTS

Since the results described were all obtained on rubber which was at one time dissolved or highly dispersed in a solvent, some idea as to the properties of the rubber particles in solution or dispersion will be of value in the interpretation of the observations. When rubber is dissolved or dispersed in a solvent, presumably small particles of rubber are freed from the mass and move about in the solvent by Brownian motion. It is a matter of definition whether these particles are designated as molecules or colloidal particles. We shall refer to them simply as particles since a detailed description of their structure is not possible. In terms of current concepts of rubber structure, they may be considered as tangles of polyisoprene chains.

When a solution of sol rubber is spread on water and the solvent is evaporated, the suspended particles aggregate to form a plastic, almost fluid film. The nodules appearing on fibers from this fraction are essentially a demonstration of the plasticity of the material. Apparently they represent regions of considerable fluidity resulting from weak interaction between the component

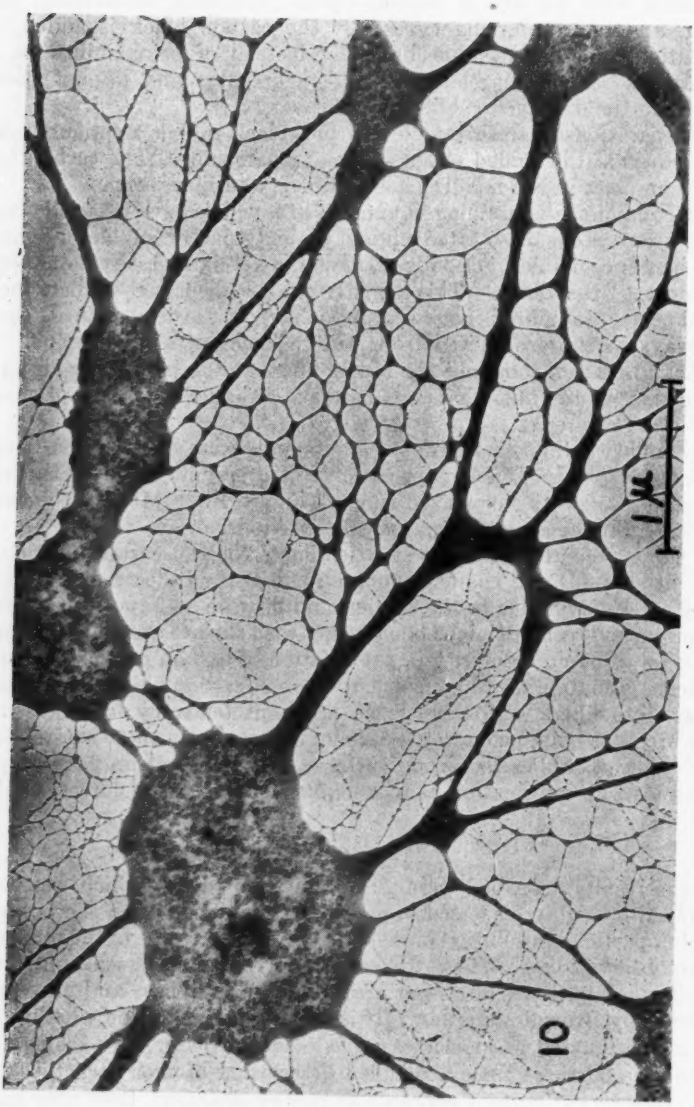

FIG. 10.—Hevea rubber containing channel black, vulcanized in solution (× 23,000).

polyisoprene chains. Intermingled with these regions are chains with sufficiently strong attachment to provide support for the fiber.

Films produced from gel fractions are strong and elastic, and electron microscope observation of specimens produced from them show fibrous networks but no nodules. In some preparations the rubber is not completely dissolved, but should properly be considered as a dispersion. In these preparations the highly branched networks seen in the electron microscope may have been produced from highly solvated networks rather than from dissolved particles. Typical gel networks have, however, been formed from clear solutions, obtained by diffusion of rubber into benzene or hexane, in which no evidence of extensive solvated networks could be found. The present evidence indicates that the gel networks seen in the electron microscope can be produced by aggregation of rubber particles on removal of the solvent and are not necessarily formed from solvated networks in solution.

Since the sol and gel solutions produce fibers with markedly different structure, it follows that the particles of the two fractions in solution must differ in important respects. It is well known that the two fractions differ in molecular weight (or particle size) as determined from viscosity measurements, but it is not immediately evident how this alone can account for the difference in fiber structure. Probably a more important difference lies in the degree of linkage between chains within the particles, and between the chains of adjacent particles on removal of the solvent.

Further evidence that a high degree of cross-linkage in the dissolved rubber particles results in fibrous networks is provided by the observations on vulcanized rubber. Before vulcanization, these solutions produce typical sol-like fibers. But when additional cross-linkage is provided by vulcanization (as is commonly supposed), the films form fibrous networks which are almost indistinguishable from those obtained from the gel fraction. Although the chemical bonding is probably different in gel and vulcanized rubber, there must be important similarities in the way in which the chains are linked together in the two cases.

Vulcanization in dilute solutions presents some interesting but poorly understood aspects. There is apparently no extensive aggregation of the rubber particles in solution unless the concentration is high enough to produce gelation. It is necessary, therefore, to explain how these particles can aggregate to form tough coherent films and fibers when the solvent evaporates. If the particles in solution have the properties characteristic of vulcanized rubber in the bulk, they would not stick together, for vulcanized rubber is not generally considered to be tacky. If the particles are joined by adhesion of unvulcanized portions, it would be expected that the agglomerates could be broken apart again by solvent action. Well vulcanized films or gels, however, are insoluble, once the original solvent has been removed. These effects indicate that, in solution, the sulfur combination is not the same as in bulk; it may be that complete combination of rubber and sulfur does not occur if the particles are highly solvated.

The beaded appearance of the fine fibers of gel rubber and those of weakly vulcanized rubber seem to represent some inhomogeneity of structural organization of the order of 200 to 500 Å. in diameter. The electron microscope gives no information at present as to the nature of these structures, but in the light of current theories a tentative explanation may be offered. The work of Mark[9], James and Guth[10], and others strongly supports the general concept that rubber consists, at least in part, of a tangle of long polyisoprene chains

which are linked together at intervals along their lengths. The segments between points of attachment are believed to have considerable freedom of rotation and, in the absence of sufficient force to keep them extended, tend to assume a disordered configuration as the most probable state statistically. The application of tension has the effect of straightening and aligning some chains, resulting in crystalline regions intermingled with others of relative disorder. A fiber would be expected to appear knotted and irregular if its diameter were of a size comparable with that of the ordered and disordered regions. Thus beads in the electron micrographs could be interpreted as small regions of relatively randomly oriented chains; the constricted, less dense portions between beads would represent regions of relative alignment due to tension on the fiber.

The coarser fibers obtained from well vulcanized solutions shown in Figure 7 could be interpreted in the same way except that the greater size of the beaded structure displayed by these fibers is undoubtedly caused by the higher degree of vulcanization (1.0 to 1.5 per cent combined sulfur). The fibers seem to consist of an end-to-end aggregation of particles of about 700 Å. diameter, within which there is so much internal bonding that they tend to retain their shape after aggregation. Between the dense beads are less dense portions of variable length, suggesting that material is pulled out from the beads by the various tensions imposed on the fibers.

Finally, some deductions may be offered from the electron micrographs concerning the nature of reënforcement with carbon black. The fact that carbon particles always appear to be surrounded by rubber indicates that rubber has an affinity for the carbon surfaces which provide points of attachment for rubber chains. Presumably, the constraints resulting from this attachment extend for some distance beyond the carbon surface, according to the amount of interaction between adjacent chains. Since the physical properties of rubber, particularly the modulus, depend to a large extent on the relative freedom of long-chain segments, any restriction caused by attachment would be expected to result in a stiffening of the material in the regions so affected. Under optimum conditions, therefore, the modulus of rubber in bulk depends on the fraction of the total rubber which lies within the influence of carbon surfaces.

It is beyond the scope of the present paper to develop this suggestion further, but some of the factors on which a quantitative treatment would depend may be mentioned. Of primary importance would be the effective distance beyond the carbon surface to which the constraints extend, together with some estimate as to how the constraints alter mobility and mean chain length in this region. Solutions of rubber containing carbon black, when examined on a collodion film (Figure 8), show a layer of rubber 100–500 Å. in thickness around the carbon particles. It is not certain from present evidence that the carbon particles effectively influence the rubber over distances of this magnitude.

The effect on bulk modulus depends on the relative amount of the rubber situated within the influence of carbon surfaces, hence on the total surface available. This, in turn, depends on the particle size, degree of dispersion, and state of aggregation of the carbon particles. In the final analysis, the important factor is the average distance between carbon particles, or the size of the rubber regions between carbon surfaces. If nearly all the rubber is in close proximity to the carbon surface, as is the case with fine reënforcing blacks, a gross effect on the bulk modulus is to be expected. If most of the rubber is remote from the regions of constraint, this part of the rubber can be expected to behave, for the most part, as though no carbon were present. Further study

with the electron microscope and correlation with data from physical tests is required to test the validity of these concepts.

SUMMARY

Hevea rubber fibers suitable for observation in the electron microscope were prepared from thin films produced by spreading rubber solutions and dispersions on a water surface. Fibers of guayule, Cryptostegia, Neoprene, and Buna-S were prepared in a similar manner and studied with the electron microscope.

Unvulcanized Hevea rubber was separated into sol and gel fractions. Electron micrographs of the sol fraction show fibers bearing many large nodules along their lengths. The spherical shape of many of the nodules is strongly suggestive of fluid properties. The gel fraction shows practically no nodules, but tends to form closely branched networks. The smallest fibers have a characteristically beaded appearance which may be related to the state of aggregation of the isoprene chains.

When pale crepe or smoked sheet is worked on the mill, cross-linked networks of the gel fraction disappear, and the milled material takes on the appearance typical of the sol. Vulcanization of milled rubber in solution has the effect of producing cross-linked networks of fine fibers similar to those from the gel fraction.

Unvulcanized and vulcanized compounds containing carbon black were examined. From the location and distribution of the carbon in rubber particles, films, and fibers, suggestions are offered concerning the nature of the reënforcement phenomena.

ACKNOWLEDGMENT

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REFERENCES

[1] Ardenne and Beischer, *Kautschuk* **16**, 55 (1940); RUBBER CHEM. TECH. **14**, 15 (1941); Morton, *RCA Rev.* **6**, No. 2, 131 (1941); Prebus, Ohio State Univ., *Eng. Exptl. Station News* **14**, No. 3, 6 (1942).
[2] Columbian Carbon Co., "Columbian Colloidal Carbons", Vol. II, 1940; RUBBER CHEM. TECH. **14**, 52 (1941); Heering, Gizycki and Kirseck, *Kautschuk* **17**, 55 (1941); Schoon and Koch, *Kautschuk* **17**, 1 (1941); RUBBER CHEM. TECH. **14**, 920 (1941); Wiegand and Ladd, *Rubber Age* (N. Y.) **50**, 431 (1942); RUBBER CHEM. TECH. **15**, 664 (1942).
[3] Weber, *Bér.* **33**, 779 (1909); Caspari, *J. Soc. Chem. Ind.* **32**, 1041 (1913); Feuchter, *Kolloidchem.-Beih.* **20**, 434 (1925).
[4] Pummerer and Pahl, *Ber.* **60**, 2152 (1927); Pummerer, Andriessen and Gündel, *Ber.* **61**, 1583 (1928); RUBBER CHEM. TECH. **2**, 367 (1929).
[5] Kemp and Peters, *J. Phys. Chem.* **43**, 923, 1063 (1939); *Ind. Eng. Chem.* **33**, 1391 (1941).
[6] Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940); RUBBER CHEM. TECH. **14**, 1 (1941).
[7] Peachey and Skipsey, *J. Soc. Chem. Ind.* **40**, 5T (1921); Peachey, *India-Rubber J.* **63**, 427 (1922).
[8] Am. Soc. Testing Materials, Standards on Rubber Products, 1943.
[9] Mark, *Ind. Eng. Chem.* **34**, 449 (1942); RUBBER CHEM. TECH. **15**, 452 (1942).
[10] James and Guth, *J. Chem. Physics* **11**, 455 (1943).

PSEUDO-PLASTIC PHENOMENA WITH VULCANIZED RUBBER*

A. J. WILDSCHUT

INTRODUCTION. FLOW AND RELAXATION

Although by the process of vulcanization, rubber is transformed from a preponderantly plastic into a preponderantly elastic, nonplastic state[1], a certain amount of plasticity always remains. For practical used this plasticity can be neglected in most cases; in other cases, however, and also from a scientific point of view, it may be desirable to know the exact amount of this deviation from the purely elastic state. A very simple and convenient method to determine this is to measure the permanent set, *i.e.*, the residual elongation after certain periods of stretching and recovery. But since the plastic properties are strongly dependent on temperature and elongation, this is not sufficient for scientific investigations, and measurements of length and tension of a given piece of rubber as a function of time and temperature are necessary.

Although it is difficult to keep the proper conditions for the experiments exactly constant, the best practical definition[2] of flow on stretching is the increase in length of a given piece of stretched rubber at constant tension[3] with increasing time. The relaxation is defined as the decrease of the tension at constant length with increasing time. By expressing length and tension in relative units, the influence of the dimensions of the test-piece can be eliminated, but the dependence on time remains, and explains why most investigators were obliged to use an arbitrary definition of the flow. As these definitions are seldom identical, it is mostly impossible to compare the results which are given in the relevant rubber literature.

By expressing flow and relaxation independently of the time, as is done in the next section, this difficulty can be eliminated.

It has been found that the rate of flow of vulcanized natural rubber strongly decreases with increasing temperature. This rather unexpected phenomenon can be explained by considering the influence of time on crystallization and of crystallization on elastic tension. For that reason in this article, after a definition of the rate of flow, crystallization as a function of time and the influence of crystallization on elastic tension are treated, leading to a definition of pseudo-flow and showing the influence of the temperature on this pseudo-flow. The decrease in the total rate of flow with increasing temperature is a consequence of the existence of pseudo-flow.

FLOW AND RELAXATION AS FUNCTION OF THE TIME

When the relative length of a piece of vulcanized rubber, after loading to a certain amount of stretching, is plotted against the time—whether seconds, hours or days—a curve is obtained as shown in Figure 1.

When a loaded piece of rubber flows, the actual cross-section diminishes, causing an increase in tension. Usually this increase is neglected; it will be shown later in which way it is possible to eliminate this error.

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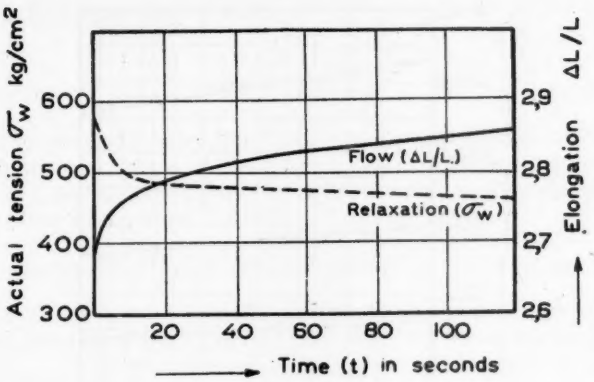

FIG. 1.—Flow and relaxation as a function of the time.

Relaxation shows the same course as flow, but, naturally, in the opposite direction.

These flow- and relaxation-time curves are not very convenient to work with; it is much simpler to plot the relative length and the tension against the logarithm of the time. As is shown in Figure 2 and Figure 3, approximately straight lines are then obtained.

The mixture used was as follows: first-latex crepe 100, diphenylguanidine 0.5, mercaptobenzothiazole 0.8, sulfur 1.75, zinc oxide 5.0, stearic acid 1.0, aldol 1.0. Cure 20 minutes at 142° C in a press.

The slopes of the lines of Figures 2 and 3 are independent of the time; the

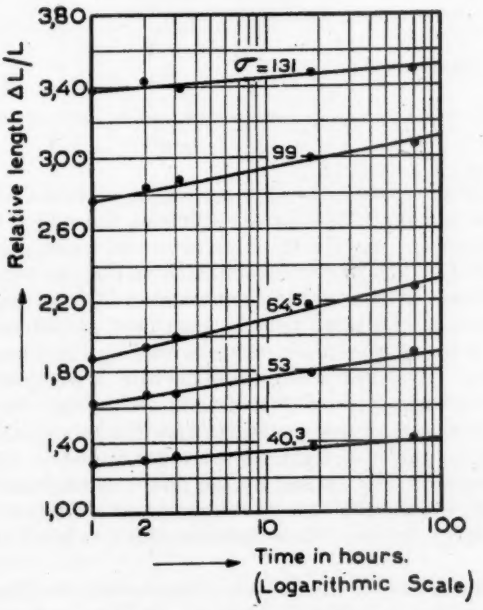

FIG. 2.—Relative length against lg t.

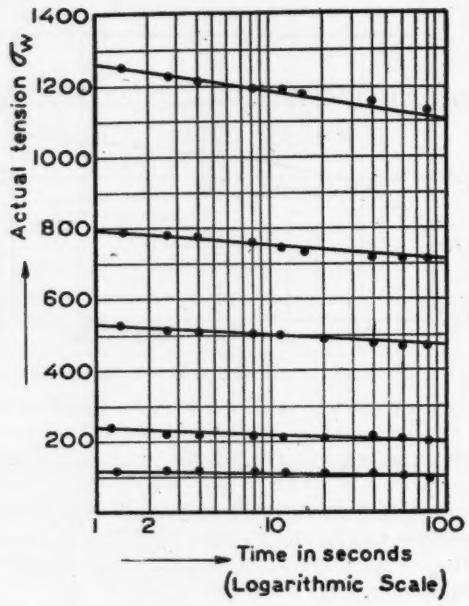

FIG 3.—Actual tension against lg t.

rate of flow v can therefore be defined as:

$$v = \frac{\Delta_2 L/L - \Delta_1 L/L}{\lg t_2 - \lg t_1} \tag{1}$$

and the rate of relaxation r as:

$$r = \frac{\sigma_{w.1} - \sigma_{w.2}}{\lg t_2 - \lg t_1} \tag{2}$$

Now with time eliminated, the only remaining variables are the actual tension in the rubber and the temperature. Plotting the rate of flow and the rate of relaxation against the actual tension gives curves which completely describe the plastic behavior of the rubber investigated at a given temperature.

When flow is measured at a sufficient number of tensions, it is possible to combine the points of the same tension, measured at different times, and so to eliminate the increase in actual tension caused by the decrease of the cross-section on flowing. This can easily be done with a wedge-shaped test-piece, and the first curves have indeed been determined in this way. As, however, measurements on series of strips proved to give the same pictures as those obtained with wedges, the investigations were continued in this way, and the increase in tension indirectly caused by the flow was neglected[4].

The measurements on the rate of relaxation at different tensions are still in a preliminary stage; in this article the rate of flow is more in particular dealt with.

The logarithmic course of the flow on compression of vulcanized rubber has been already described in rubber literature. Badum and Leilich[5], who have

measured this flow, give the formula:

$$p = \frac{H_0 - H_t}{\lg t/t_0} \tag{3}$$

in which p is the rate of flow on compression and H_0 and H_t are the heights of a test-piece under compression at the times t_0 and t. Formula (3) is analogous to Formula (1); there is no difference in behavior of vulcanized rubber when stretched or when compressed.

THE RATE OF FLOW AS A FUNCTION OF THE TENSION

When the rate of flow (v), as defined by Formula (1), is measured at increasing actual tension (σ_w) and v is plotted against σ_w, the result is a curve as shown in Figure 4.

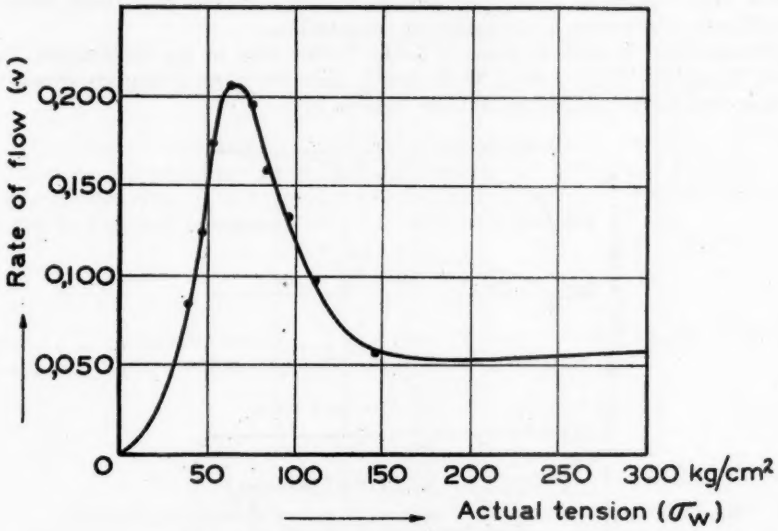

FIG. 4.—$\sigma - v$ diagram of vulcanized natural rubber[5] at 20° C.

The sharp maximum in this curve is remarkable; it lies at about 65 kg./per sq. cm. actual tension, which corresponds to an elongation of about 300 per cent. It is clear that this phenomenon is caused by the crystallization of the rubber, which obviously at 300 per cent elongation has already enough influence to make a further increase of the rate of flow impossible. An increase in actual tension of about 100 kg./per sq. cm., corresponding to an increase in elongation of only 100 per cent, is required to bring the rate of flow back to about a quarter of the maximum. At still higher elongations the rate of flow increases a little; shortly before break—which in this case occurs at 700–750 per cent—the rate of flow seems to increase somewhat more, but measurements in this region are very difficult, as the rubber can stand these elongations only for a comparatively short time.

A similar effect has been found by Treloar[6] for the permanent set of unvulcanized rubber, and by Field[7] for the flow of vulcanized rubber. Field still

gives an arbitrary definition of the flow. He uses the word creep, and the concept of the rate of flow was not introduced, thus making an accurate comparison impossible.

According to Hauk and Neumann[8], Kirsch[9] was the first to describe the phenomenon.

CRYSTALLIZATION AND ANISOTROPY AS A FUNCTION OF THE TIME

For a good understanding of the next paragraph, a discussion of the effect of time on the crystallization and of crystallization on the elastic tension is necessary.

Thiessen and Wittstadt[10] measured the degree of orientation of the rubber molecules by determining the optical anisotropy at different elongations and temperatures as a function of time. They suppose crystallization to run parallel to optical anisotropy, and it is very likely that at least the orientation increases with increasing anisotropy and that, with vulcanized natural rubber, crystallization increases with increasing orientation.

Thiessen and Wittstadt found a distinct aftereffect of the orientation; the curves, some of which are given in Figure 5, resemble those giving the course of the flow and the relaxation with time (Figure 1).

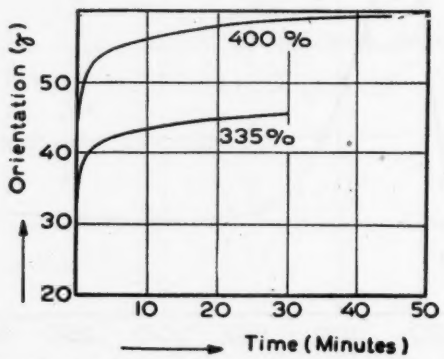

FIG. 5.—Orientation as a function of the time. Vulcanized natural rubber[11] at 20° C. After Thiessen and Wittstadt[10].

From Figure 5 it can be seen that, after stretching, crystallization does not immediately reach its maximum, but increases, rapidly at first, more slowly afterwards, to a top value. Considering the shape of the curves of Figure 5, it is not unlikely that also in this case a logarithmic course is followed approximately. From Figure 6 it follows that this crystallization aftereffect rapidly diminishes with increasing temperature.

More directly still the crystallization aftereffect was shown by Holt and McPherson[12], who measured the decrease in volume of stretched vulcanized rubber with the time. On stretching a pure-gum mixture, the volume decreases, owing to crystallization. The rubber being stretched, however, this decrease goes on, following an approximately linear course with the logarithm of the time.

The effect found by Meyer and Ferri[13], though given in a different way, is based on the same phenomenon. It is shown by Figure 7, in which the relation between the elastic tension and the temperature for constant elongation is given.

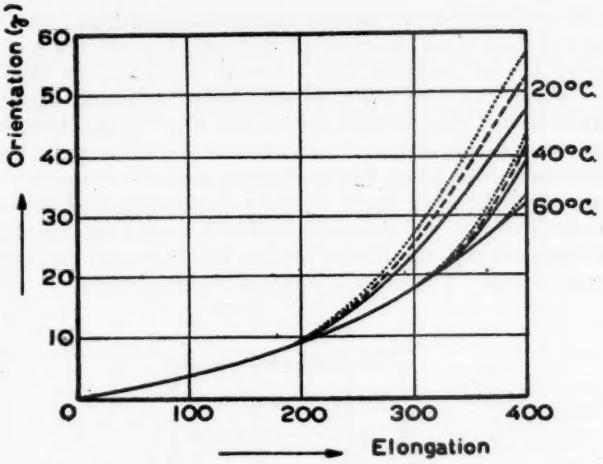

FIG. 6.—Influence of the temperature on the orientation-after-effect. —— measured after 10 seconds, — — — — after 1 minute, ... after 5 minutes. After Thiessen and Wittstadt[10].

If a strip of vulcanized rubber is kept under constant elongation at 70° C till the tension no longer diminishes for a few hours (point a of Figure 7), and is then cooled down rather rapidly, a straight line ($a \rightarrow b$) is obtained, according to the well-known formula[14]:

$$\sigma = \left(\frac{\partial U}{\partial L}\right)_T + T\left(\frac{\partial \sigma}{\partial T}\right)_L \qquad (4)$$

where σ is the elastic tension, U the internal energy, L the length of the test-piece and T the absolute temperature.

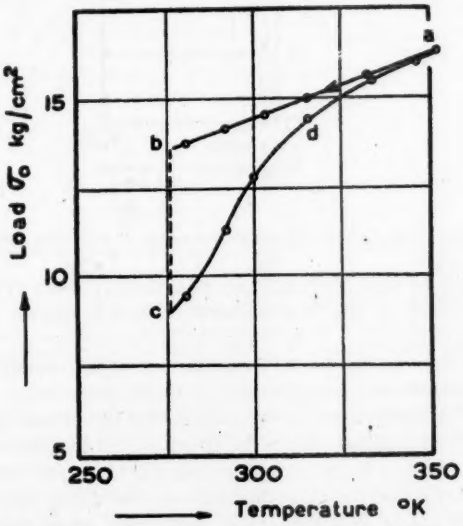

FIG. 7.—Relation of load to absolute temperature. Vulcanized natural rubber: crepe 100, zinc oxide 3, sulfur 5, diphenylguanidine 1. Cure 30 minutes at 147° C in a press. After Meyer and Ferri[13].

If at b the rubber is kept under constant elongation and at constant temperature for a certain time, the elastic tension diminishes in a way which from outside cannot be distinguished from normal relaxation, so that the point c is reached. When, however, the stretched rubber is heated again, the tension increases more rapidly than corresponds to the slope of the straight line $a \rightarrow b$, so that at about d the tension all but reaches its old value in the line $a \rightarrow b$ and at a has come back completely to the starting point.

The same effect has been found by the present author[16], also on measuring in the opposite direction. If stretched rubber is heated and cooled down again to the same temperature, the elastic tension has increased and only gradually reaches the old value. The process is, of course, reversible.

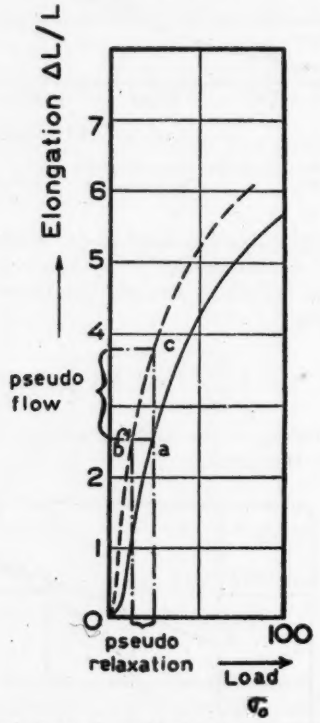

FIG. 8.—Pseudo-flow and pseudo-relaxation of vulcanized rubber.

The explanation of this phenomenon has already been given by Meyer and Ferri[13]; an after-effect of the crystallization, which causes a decrease of the elastic tension.

The fact that the elastic tension diminishes with increasing crystallization at constant elongation and temperature is quite clear from a thermodynamic point of view. The elastic force being caused by the thread molecules, striving for higher entropy, or a higher degree of freedom, diminishes when part of these molecules combine into a crystal lattice and thus are put out of action. The same conclusion is reached on considering Formula (4); at increasing crystallization the term $(\partial U/\partial L)_T$ becomes more negative, and, the term $T(\partial\sigma/\partial T)_L$ remaining constant, σ must decrease.

PSEUDO-RELAXATION AND PSEUDO-FLOW

If, bearing the preceding paragraph well in mind, we consider the situation which occurs when a piece of perfectly elastic rubber is stretched rapidly and is then kept under constant elongation, we obtain a picture which is illustrated by Figure 8.

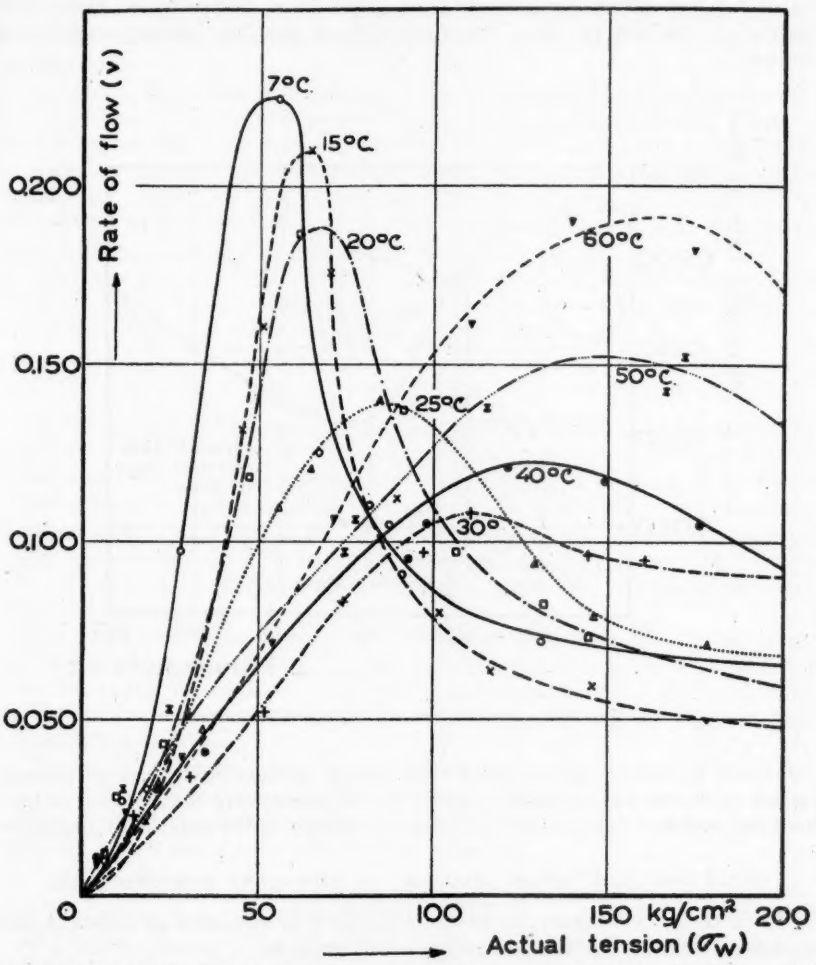

FIG. 9.—Tension-rate of flow diagrams at different temperatures. Vulcanized natural rubber: crepe 100, diphenylguanidine 0.5, mercaptobenzothiazole 0.8, sulfur 1.75, zinc oxide 5.0, stearic acid 1.0, aldol 1.0. Cure 20 minutes at 142° C in a press.

Starting from the origin and following the drawn curve, the point a is reached. A certain crystallization has then taken place, increasing with time. As a result, the tension decreases and, the elongation being constant, after a certain time the point b is reached. The decrease in tension $a - b$ is measured as relaxation; the phenomenon being reversible, however, and, in rubber technology, flow and relaxation being considered plastic properties, this relaxation

must be clearly distinguished from the normal one, and therefore is called *pseudo-relaxation.*

When, after stretching to the point *a*, the rubber is kept under constant load, it is impossible for the tension to decrease, and the only way to reach equilibrium is an increase in the elongation till the point *c* on the dotted curve is reached. This increase in elongation, which, especially in the first part of the load-elongation curve, can be very considerable is measured as flow. Distinguishing this sort of "flow" from the normal flow, the name *pseudo-flow* is proposed.

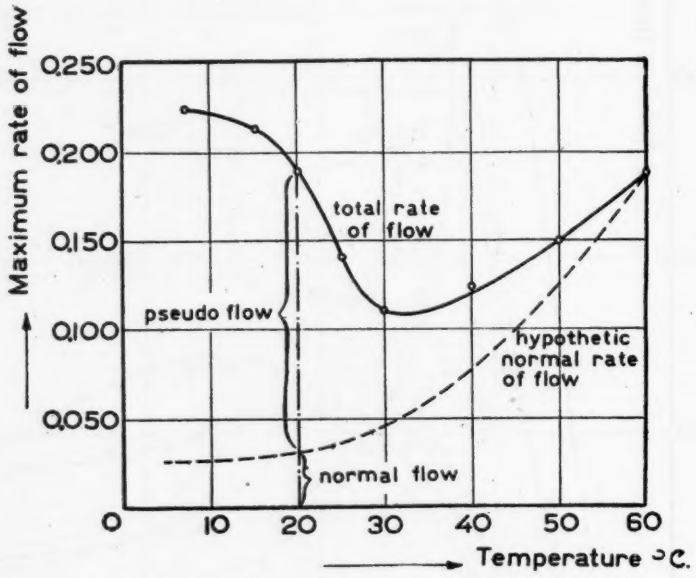

FIG. 10.—Maximum rate of flow as a function of the temperature.

As can be seen from Figures 6 and 10, the pseudo-flow must be strongly dependent on the temperature. At 20° C the pseudo-flow may be two or three times the real flow, while at 60° C the pseudo-flow may be practically negligible.

TENSION-RATE OF FLOW DIAGRAMS AT DIFFERENT TEMPERATURES

When the σ—v-diagram, as given in Figure 4, is measured at different temperatures, curves are obtained as shown in Figure 9.

From Figure 9 it can be seen that the maximum rate of flow rapidly decreases with increasing temperature, passes through a minimum, and then increases again till at 60° C the value of about 20° C is reached. Figure 9 also shows the rather striking fact that practically no yield value has been found; even at very low tensions and elongations the rate of flow is easily measurable.

By plotting the maximum rate of flow against the temperature the decrease in rate of flow with increasing temperature is shown more clearly in Figure 10.

The curves of Figures 9 and 10 can be understood only if we suppose the

flow to be composed of normal flow and pseudo-flow, so that we can write:

$$\text{total flow} = \text{normal flow} + \text{pseudo-flow}$$

The normal flow, caused by the residual plasticity of the material, increases with increasing temperature. As is shown in the preceding paragraphs, however, the pseudo-flow diminished with increasing temperature. The result is that, from 7 to 30° C, in which region the pseudo-flow appears to play the most important role, the total flow decreases, notwithstanding the increase of the normal flow.

Following the curve from Figure 10 from higher to lower temperatures, at 60° C we may suppose the pseudo-flow to be negligible (compare Figure 6). At this temperature the total flow becomes equal to the normal flow. Let the normal flow decrease at decreasing temperature according to the hypothetic dotted line. Then at each temperature an idea is given of the ratio of the normal flow to the pseudo-flow. At room temperature the pseudo-flow may be several times stronger than the normal flow.

This throws new light on the important property of flow on stretching vulcanized rubber, and shows that at room temperature the deviation from the purely elastic state is still far less than is generally thought.

CONCLUSIONS

As the flow on stretching vulcanized rubber appears to follow a logarithmic course with time, it is possible to obtain data on the rate of flow which are independent of time. Plotted against the actual stress or the elongation, the rate of flow passes through a maximum, caused by the influence of crystallization. It can be proved that part of the total flow measured is caused by a retardation in the crystallization. This part of the flow is reversible, and is called pseudo-flow. An analogous situation occurs with the relaxation, and is called pseudo-relaxation.

The total flow, measured at room temperature, may consist for the greater part of pseudo-flow, the normal flow then being but a minor fraction of it. With increasing temperature, the normal flow increases, but the pseudo-flow rapidly decreases. As a result, the total flow passes through a minimum with increasing temperature.

The study of tension-rate of flow diagrams is useful in extending our insight into the influence of the crystallization on the properties of vulcanized rubber.

The investigations are being continued by carrying out measurements on synthetic rubber and by a study of the relaxation.

ACKNOWLEDGMENT

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SUMMARY

It is shown that plastic flow and relaxation of vulcanized natural rubber follow a logarithmic course with time. As a result, it is possible to define *rate of flow* as the ratio of flow at constant tension to the logarithm of the time, and *rate of relaxation* as the ratio of the decline in tension at constant elongation to the logarithm of the time.

A study of tension-rate of flow diagrams at different temperatures has shown that, at room temperature, a considerable part of the total flow measured is reversible and therefore must be considered as pseudo-flow. This pseudo-flow is caused by a retardation in crystallization, and diminishes with increase in temperature. As a result, with increasing temperature, the total rate of flow passes through a minimum. An analogous situation occurs with the phenomenon of relaxation.

REFERENCES

[1] Wildschut, *Rec. trav. chim.* **61**, 899 (1942).
[2] Without any doubt, a better one is the rate of shear at constant tension, but measurements with vulcanized rubber in a rotation plastometer are still lacking.
[3] The tension is defined as the ratio of the load to the actual cross-section. See also Wildschut, *Physica* **10**, 65 (1943); Rubber Chem. Tech. **17**, 826 (1944).
[4] Minor difficulties have compelled us to abandon the use of wedges. These wedges were divided, for example, into 40 parts of 1 mm. length, and the flow of each part was measured with a precision cathetometer. It was necessary to measure a very short length, making it possible to work with a mean tension. With the cathetometer, which has been specially built for this purpose (by C. Bleeker, Utrecht, Holland) this was comparatively easy, but the vulcanizing of the wedge so as to be absolutely homogeneous was not so easy. When this was not the case, the elongation of the wedge was irregular, and the calculation of the actual tension inaccurate. Besides, at higher elongations, the two marks limiting a segment were elongated in different ways, giving rise to new errors.
[5] Prepared from the mixture: first-latex crepe 100, sulfur 1.75, mercaptobenzothiazole 0.8, diphenylguanidine 0.5, stearic acid 1.0, aldol 1.0, zinc oxide 5; cured 20 min. at 142° C in a press.
[6] Treloar, *Trans. Faraday Soc.* **36**, 538 (1940).
[7] Field, *J. Applied Physics* **12**, 43 (1941).
[8] Hauk and Neumann, *Monatsh.* **72**, 22 (1938).
[9] Kirsch, Thesis, Berlin, 1937.
[10] Thiessen and Wittstadt, *Z. physik. Chem.* **B41**, 33 (1938).
[11] Vulcanized rubber with 93.8 per cent rubber hydrocarbon. Further data concerning the composition and cure are not given.
[12] Holt and McPherson, *J. Research Natl. Bur. Standards* **17** (1936).
[13] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935).
[14] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1934); Wöhlisch, *J. prakt. Chem.* **160**, 217 (1942).
[15] Wildschut, unpublished investigations.

THEORY OF FILLER REËNFORCEMENT IN NATURAL AND SYNTHETIC RUBBER. THE STRESSES IN AND ABOUT THE PARTICLES *

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The mechanism by which finely divided fillers, notably carbon black, give rise to greatly improved mechanical properties of rubber compounds has been the object of many investigations. The extensive literature on this subject has been reviewed rather recently by Hock[1], and also by Shepard, Street, and Park[2]. The great majority of that work and the theories derived therefrom are based on results obtained with natural rubber. Briefly stated, the two factors most generally invoked to explain filler reënforcement are (at least for more or less spherical particles): (1) the specific surface-area of the particles, and (2) the strength of the bond, or interfacial energy, at the filler-rubber boundary. Yet, it is a matter of common experience that when an effort is made to apply such information or theory to synthetic rubbers, one encounters irregularities that are little understood and are often attributed to factor (2). It seems reasonable to expect that a satisfactory theory of filler reënforcement should be equally applicable, not only to fillers of varying specific surface-area and composition, but also to a variety of natural and synthetic rubbers. Furthermore, while one can hardly deny that the strength of the filler-rubber interface is an important factor in reënforcement behavior, the older theories do not make it evident how this bonding brings about reënforcement. It is, therefore, desirable to develop a general theory of filler reënforcement that has greater mechanistic clarity.

In a recent attempt of this sort, Weiss[3] considered the total increase in free energy due to filler to consist of two parts: (1) the total surface free energy F_s of the particles in the mixture, and (2) the total elastic energy F_e set up in the matrix by the filler. In common with earlier workers[4] he suggested that information on F_s might be obtained by measuring the heat of wetting of fillers by organic liquids. To give expression to the elastic energy contribution, Weiss applied a theory developed by Mott and Nabarro[5] for the case of precipitation hardening in metals. The physical concept involved in his treatment is that a particle of filler imbedded in rubber generally has a different volume from the actual space (or "hole") in the material available for it. If it is held firmly enough by the surface forces, the particle compresses or expands the surrounding medium, depending on whether it is larger or smaller than the "hole" in the matrix, and thus set up a more or less symmetrical stress field. Although Weiss's treatment is valuable in emphasizing the necessity for considering the stress field, it has the disadvantages of introducing a rather arbitrary "hole" parameter, and, what is more important from the standpoint of rubber be-

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havior, it does not show how the internal stresses depend on the degree of deformation or on the magnitude of an applied force. In a treatment independently worked out by the writer, and presented below, an attempt is made to develop this subject and to point out its bearing on the general problem of reënforcement.

THE STRESSES NEAR SPHERICAL INCLUSIONS IN ELASTIC MEDIA

The problem here considered is that of determining the stresses in the neighborhood of a spherical particle of radius a imbedded in an elastic medium of infinite extent, the latter being subjected to a uniform tension T at infinity. It is assumed that the particle is rigidly attached to the adjacent layer of the elastic medium, and that the latter is subjected only to infinitesimal deformations. It is then possible to apply the results of the classical theory of elasticity. The general equations of equilibrium of an elastic body[6], expressed in spherical coordinates and omitting the azimuthal component of motion, may be written:

$$(\lambda + 2\mu)\frac{\partial \Delta}{\partial r} - (2\mu/r)\frac{\partial \tilde{\omega}}{\partial \theta} - (2\mu/r)\tilde{\omega}\cot\theta = 0$$

$$[(\lambda + 2\mu)/r]\frac{\partial \Delta}{\partial \theta} + 2\mu\frac{\partial \tilde{\omega}}{\partial r} + 2\mu\tilde{\omega}/r = 0 \qquad (1)$$

where λ and μ are Lamé's elastic constants, u and v are the radial and colatitudinal components of displacement, and:

$$\Delta = \frac{\partial u}{\partial r} + 2\mu/r + (1/r)\frac{\partial v}{\partial \theta} + (v/r)\cot\theta$$

$$2\tilde{\omega} = \frac{\partial v}{\partial r} + v/r - (1/r)\frac{\partial u}{\partial \theta} \qquad (2)$$

These equations were solved for the case of an imbedded spherical particle by Sezawa and Miyazaki[7] to a degree of approximation including the second order of spherical harmonics, omitting terms of polar unsymmetry and terms which would make the stresses at infinity very large. Since their calculations appear to have been completely overlooked, probably because of general inaccessibility, the complete results of their solution are given below. Denoting the elastic constants of the particle by accents, those of the surrounding medium being unaccented, the stress components within the sphere were found to be:

$$p_{rr}'/T = (\lambda + 2\mu)(3\lambda' + 2\mu')/(3\lambda + 2\mu)(3\lambda' + 2\mu' + 4\mu) + (4\mu' D_1/D)P_2(\cos\theta) \qquad (3a)$$

$$p_{\theta\theta}'/T = (\lambda + 2\mu)(3\lambda' + 2\mu')/(3\lambda + 2\mu)(3\lambda' + 2\mu' + 4\mu) + 2\mu' D_1/D - (4\mu' D_1/D)P_2(\cos\theta) \qquad (3b)$$

$$p_{\phi\phi}'/T = (\lambda + 2\mu)(3\lambda' + 2\mu')/(3\lambda + 2\mu)(3\lambda' + 2\mu' + 4\mu) - 2\mu' D_1/D, \qquad (3c)$$

$$p_{r\theta}'/T = (2\mu D_1/D)\frac{dP_2(\cos\theta)}{d\theta} \qquad (3d)$$

The stresses in the medium are given by the relations:

$$p_{rr}/T = 1/3 + \{4\mu[3(\lambda' - \lambda) + 2(\mu' - \mu)]/(3\lambda + 2\mu)(9\lambda' + 6\mu' + 12\mu)\}(a^3/r^3) + \{2/3 + [(9\lambda + 10\mu)D_2/3D](a^3/r^3) + (24\mu D_3/D)(a^5/r^5)\}P_2(\cos\theta), \tag{4a}$$

$$p_{\theta\theta}/T = 2/3 - \{2\mu[3(\lambda' - \lambda) + 2(\mu' - \mu)]/(3\lambda + 2\mu)(9\lambda' + 6\mu' + 12\mu) + \mu D_2/3D\} \times (a^3/r^3) + (2\mu D_3/D)(a^5/r^5) - \{2/3 + (\mu D_2/3D)(a^3/r^3) + (14\mu D_3/D)(a^5/r^5)\}P_2(\cos\theta) \tag{4b}$$

$$p_{\phi\phi}/T = \{\mu D_2/3D - 2\mu[3(\lambda' - \lambda) + 2(\mu' - \mu)]/(3\lambda + 2\mu)(9\lambda' + 6\mu' + 12\mu)\}(a^3/r^3) - (2\mu D^3/D)(a^5/r^5) - \{(\mu D_2/D)(a^3/r^3) + (10\mu D_3/D)(a^5/r^5)\}P_2(\cos\theta) \tag{4c}$$

$$p_{r\theta}/T = \{1/3 - [(3\lambda + 2\mu)D_2/6D](a^3/r^3) - (8\mu D_3/D)(a^5/r^5)\}\frac{dP_2(\cos\theta)}{d\theta} \tag{4d}$$

where $P_2(\cos\theta)$ is the Legendre function of the second degree, and the D's are functions of the elastic constants, and are given by the determinants:

$$D = \begin{vmatrix} \lambda'/7 & 4\mu' & -(9\lambda + 10\mu)/3 & -24\mu \\ -(8\lambda' + 7\mu')/21 & 2\mu' & (3\lambda + 2\mu)/6 & 8\mu \\ -\lambda'/7\mu' & 2 & (3\lambda + 5\mu)/6\mu & 3 \\ -5\lambda' + 7\mu')/42\mu' & 1 & 1/6 & -1 \end{vmatrix} \tag{5a}$$

$$D_1 = \begin{vmatrix} \lambda'/7 & 2/3 & -(9\lambda + 10\mu)/3 & -24\mu \\ -(8\lambda' + 7\mu')/21 & 1/3 & (3\lambda + 2\mu)/6 & 8\mu \\ -\lambda'/7\mu' & 1/3\mu & (3\lambda + 5\mu)/6\mu & 3 \\ -(5\lambda' + 7\mu')/42\mu' & 1/6\mu & 1/6 & -1 \end{vmatrix} \tag{5b}$$

$$D_2 = \begin{vmatrix} \lambda'/7 & 4\mu' & 2/3 & -24\mu \\ -(8\lambda' + 7\mu')/21 & 2\mu' & 1/3 & 8\mu \\ -\lambda'/7\mu' & 2 & 1/3\mu & 3 \\ -(5\lambda' + 7\mu')/42\mu' & 1 & 1/6\mu & -1 \end{vmatrix} \tag{5c}$$

$$D_3 = \begin{vmatrix} \lambda'/7 & 4\mu' & -(9\lambda + 10\mu)/3 & 2/3 \\ -(8\lambda' + 7\mu')/21 & 2\mu' & (3\lambda + 2\mu)/6 & 1/3 \\ -\lambda'/7\mu' & 2 & (3\lambda + 5\mu)/6\mu & 1/3\mu \\ -(5\lambda' + 7\mu')/42\mu' & 1 & 1/6 & 1/6\mu \end{vmatrix} \tag{5d}$$

It can be seen from Equations (3) that the stress components within the sphere are independent of the radial distance. The stresses at a given point in the surrounding medium depend on the elastic constants both of the sphere

and of the medium, as shown by Equations (4) and (5), on the radius a of the sphere, on the distance r from the center of the sphere to the point under consideration, and on the angle θ that the latter line makes with the direction of the externally applied traction (see Figure 1).

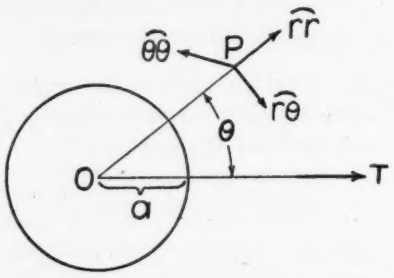

FIG. 1.

AVERAGE STRESSES DUE TO MANY INDEPENDENT PARTICLES

To make a closer examination of the stress relations, let us consider the radial stress p_{rr} in the medium at a point lying on the direction vector of the applied tension. Then $\theta = 0°$, and Equation (4a) may be written:

$$p_{rr}/T = c_1 + c_2(a^3/r^3) + c_3(a^5/r^5) \tag{6}$$

where c_2 and c_3 are functions of the elastic constants. If there are N similar particles in unit volume, and if these be sufficientiy far apart to avoid the effects of particle interactions (which will not be the case for, say, a tire-tread composition, in which the mean particle separation is comparable in magnitude to the particle diameter), then the average distance $\bar{r}$ between the centers of the particles is of the order $(1/N)^{\frac{1}{3}}$ and the average radial stress, according to Equation (6), becomes:

$$(p_{rr}/T)_{Av} = c_1 + c_2'Na^3 + c_3'(Na^3)^{5/3} \tag{7a}$$

Since the volume fraction v_f of the filler present is proportional to Na^3, the average stress may be written:

$$(p_{rr}/T)_{Av} = c_1 + c_2''v_f + c_3''v_f^{5/3} \tag{7b}$$

The first term in Equation (7b) is obviously the stress that would be obtained when tension is applied to an elastic medium containing no filler particles ($v_f = 0$), while the remaining terms represent the filler contribution. The average stress is found to have a maximum at $v_f = (-3c_2''/5c_3'')^{\frac{3}{2}}$. In this connection, it may be worth while to point out that, as is commonly known, the reënforcing properties of active fillers do not simply increase with increasing filler concentration, but pass through a maximum, whose location depends primarily on the nature of the filler (for a given kind of rubber). (It is hardly necessary to point out that Equation (7b) cannot be used to determine quantitatively the optimum filler concentration, since the latter generally occurs for such high values of N that the effects of particle interactions are, in all probability, not negligible.) The average elastic energy associated with the radial stress is proportional to $(p_{rr}/T)^2_{Av}$ and likewise has a maximum at the same value of v_f as does the average stress.

For a given direction θ (other than $\theta = 0°$), it is seen that the shear stress, Equation (4*d*), has the same form as Equation (6) (but with different values of the coefficients). The average shear stress for a system containing many particles is, therefore, given by a relationship similar to Equation (7*b*), but with a different value of the filler concentration at the maximum. In other words, the filler concentration required to give a maximum value to the average tensile stress will not, in general, coincide with that giving the maximum average shear stress.

The average radial (and likewise shear) stress is seen from Equation (7*b*) to be independent of the size of the particles, but depends only on their concentration, and on the values of the elastic constants represented by the coefficients.

APPLICATION TO NATURAL AND SYNTHETIC RUBBERS

Since the stresses in a system containing a single particle would be expected to give at least a semiquantitative insight into the mechanical behavior of many-particle systems in which the particles are not sufficiently far apart to avoid interaction, it is of interest to determine the radial dependence of the stress-components of Equations (4). Since this evaluation requires a knowledge of the elastic constants of both phases, it is unfortunate that scarcely any such data are to be found in the literature for materials used as rubber fillers, and none for synthetic rubbers.

Carbon blacks, for which no elastic constants are available, are the fillers of greatest value and interest. The bulk modulus K for graphite, according to Richards[8], is 4.9×10^6 lbs. per sq. in., presumably at room temperature. It is assumed here that the values of K for carbon blacks do not differ much from that of graphite. In view of the graphite-like nature of carbon blacks[9], this assumption seems to be reasonably good for the types of carbon blacks most commonly used as rubber fillers, but would doubtless be inadmissible for some types, the particles of which appear to have a considerable amount of porosity[10]. Furthermore, results based on this value of K should be qualitatively applicable to other kinds of fillers, since the bulk moduli of most solids are of the same order of magnitude[11] (Table I). The modulus of rigidity μ of

TABLE I

CUBICAL COMPRESSIBILITIES OF SOME SOLIDS

Material	Compressibility (sq. cm. per kg.) $\times 10^6$
Graphite	3.0
Aluminum oxide (sapphire)	0.317
Magnesium oxide (pressed powder)	0.986
Other oxides, crystalline salts, sugars, and minerals of widely different structures and compositions	0.3–19

any isotropic solid is related to K and to the Poisson ratio σ by the equation: $\mu = 3K(1 - 2\sigma)/2(1 + \sigma)$. Since σ for graphite is not given in the literature, we assume it to have a value in the normal range of 0.25–0.33. The rigidities corresponding to these limits are 2.9×10^6 and 1.8×10^6 lbs. per sq. in., respectively. It will be seen later that the resulting stresses are not appreciably sensitive to the variation thus introduced by the uncertainty in σ. Since, for an isotropic solid, $K = \lambda + 2\mu/3$, the corresponding values of λ are 3.0×10^6

and 3.7×10^6 lbs. per sq. in. To simplify the numerical calculations, rounded values of $\lambda = 4 \times 10^6$ and $\mu = 2 \times 10^6$ will be used for graphite.

From the work of Adams and Gibson[12] it is found that the value of K for vulcanized natural rubber is about 4×10^5 lbs. per sq. in. at pressures in the vicinity of one atmosphere. Since a tire-tread composition has a modulus of rigidity roughly 100 lbs. per sq. in.[13] we may use $\lambda = 4 \times 10^5$ and $\mu = 100$ as typical values for the rubber medium.

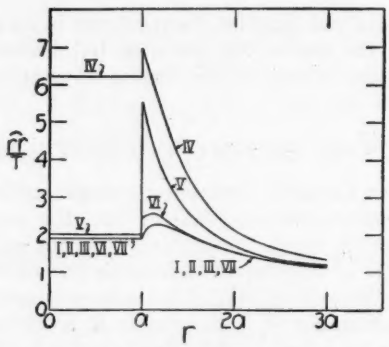

FIG. 2.—Calculated radial stress p_{rr} in and about a spherical particle as a function of distance and of the elastic constants for $\theta = 0°$. The curves are numbered in accordance with the data given in Table II.

The curves in Figure 2 show the effects of varying the values of the elastic constants on the radial stress at various distances from the imbedded particle along the direction of the applied tension $T(\theta = 0°)$. These curves were calculated by means of Equations (3a) and (4a), the elastic constants used for this purpose being tabulated, together with the corresponding values of the various determinants [Equations (5)], in Table II. The stress is observed to be

TABLE II

ELASTIC CONSTANTS AND CORRESPONDING DETERMINANTS

Curve	λ' $\times 10^{-6}$	μ' $\times 10^{-6}$	λ $\times 10^{-6}$	μ	$-D$ $\times 10^{-13}$	$-D_1$ $\times 10^{-11}$	$-D_2$ $\times 10^{-11}$	D_3 $\times 10^{-13}$
I	4	2	4	100	39.6	0.826	1.65	6.60
II	3	3	4	100	56.6	0.786	2.36	9.43
III	4	2	6	100	59.4	1.24	1.65	9.90
IV	4	2	6	50	59.4	4.38	3.30	19.8
V	1	0.5	4	100	2.48	0.206	0.103	0.0476
VI	1	0.5	4	50	4.67	0.370	0.195	1.56
VII	4	2	4	50	79.2	1.65	3.30	26.4

independent of distance within the particle ($r < a$). At the surface, the stress in the medium rises discontinuously and rapidly to a maximum, the position of which depends on the set of constants chosen, and then decreases asymptotically to the value of the applied tension. For a particle such as graphite[14] in natural rubber, a comparison of curves I and VII shows that a twofold change in the rigidity of the medium does not affect the stress. Curves I and III show that, for $\mu = 100$, a 50 per cent increase in the bulk modulus of the medium likewise has no appreciable effect on the stress. However, if this particle is imbedded in a medium the bulk modulus of which is 50 per cent greater than that of natural rubber, it is seen from curves III and IV that a twofold change in the rigidity of the medium has a large effect on the stress, the latter

being more than three times as large, at the surface of the particle, for the medium having the lower rigidity.

A comparison of curves I and II shows that the uncertainty in the value of the Poisson ratio for graphite is not reflected in any change in the stress.

If the graphite particle is replaced by one the compressibility of which is four times as large, it is observed (curve V) that the stress at the surface of the particle is increased almost threefold when $\mu = 100$ for the medium. If, on the other hand, $\mu = 50$, the increase in stress (curve VI) is much less.

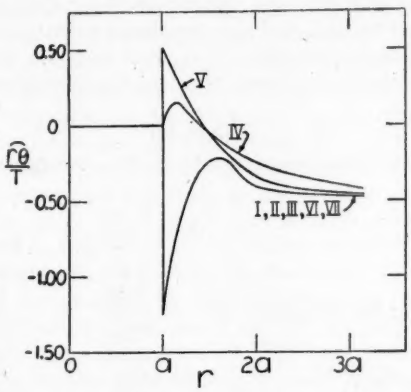

FIG. 3.—Calculated shear stress $p_{r\theta}$ in and about a spherical particle as a function of distance and of the elastic constants for $\theta = 45°$. The curves are numbered in accordance with the data given in Table II.

Figure 3 shows the behavior of the shear stress p_r as a function of the elastic constants. The curves were calculated by means of Equations (3*d*) and (4*d*) with the sets of constants given in Table II, for points on a line making an angle of $\theta = 45°$ with the direction of applied tension. It is seen that, as in the case of the radial stress, the values of the elastic constants have a considerable influence on the shear stress. Since the general comparisons are very similar to those made above for the case of the radial stress, no more detailed discussion will be made for this case.

It may be concluded that, to obtain a state of minimum stress, it is necessary to obtain a proper balance, so to speak, between the elastic constants of the imbedded particle and of the medium. The curves indicate that a series of particles possessing different values of elastic constants do not necessarily show the same order of behavior when the medium in which they are imbedded is changed. It is, therefore, of interest to consider to what extent the elastic constants of various rubberlike materials differ.

ELASTIC CONSTANTS OF SYNTHETIC RUBBERS

To make quantitative estimates of the stresses, a knowledge is required of the values of the elastic constants of both the filler and the rubber medium. The extent of variation to be expected in the case of fillers has already been considered. The maximum variation in the compressibility of solids, as shown in Table I, is about fiftyfold, and the corresponding bulk moduli will have a spread of the same order. No data are available for the elastic constants of synthetic rubbers. For the purpose of estimating the range of values that such

materials may be expected to exhibit, it is therefore necessary to resort to theoretical calculations.

The molecular sound velocity V is defined by the relation

$$v_s = (Vd/M)^3 \tag{8}$$

where v_s is the velocity of sound, d is the density, and M is the molecular weight. It has been shown[15] that, for a large number of different kinds of organic liquids, V is an accurately additive function of what have been termed "bond velocities". The latter have been determined[16] for various chemical linkages. With the aid of these values, and one supplementary bond velocity[17] that was not determined by Lagemann and Corry, it is possible to calculate by means of Equation (8) the velocity of sound in the synthetic rubbers listed in Table III,

TABLE III

CALCULATED COMPRESSIBILITY DATA FOR SYNTHETIC RUBBERS

Rubber	d	v_s(m/sec.)	Bulk modulus (lb./sq. in.) $\times 10^{-5}$
Polychloroprene	1.25	1720	5.44
Methyl rubber	0.93	1930	5.07
Polyisobutylene (or Butyl rubber)	0.92	1930	4.90
Perbunan*	0.96	1790	4.54
Buna-S**	0.94	1690	3.92
Polyisoprene	0.9	1710	3.87
Polybutadiene	0.9	1650	3.59

* Calculated for a ratio of three moles of butadiene to one mole of acrylonitrile.
** Calculated for a ratio of five moles of butadiene to one mole of styrene.

and from these results the isothermal[18] compressibilities and bulk moduli. The calculated value for polyisoprene (3.87×10^5) is in surprisingly good agreement with the experimental value (3.98×10^5) obtained by Adams and Gibson[12] for vulcanized natural rubber. Since no other experimental values are available for comparison with the remaining data of Table III, it cannot be stated with certainty whether or not this agreement for natural rubber is accidental. Since the modulus of rigidity is not a characteristic constant, but may be altered over rather wide limits by the use of various compounding ingredients and conditions of vulcanization, no values are listed for this parameter. For the synthetic rubbers considered here, it is seen that the extreme values of the bulk modulus (and therefore λ) differ by roughly 50 per cent. It was for this reason that the range of values for λ given in Table II was selected for the stress calculations.

DISCUSSION

The treatment presented in this paper serves to show that the stresses occurring in the vicinity of particles imbedded in rubberlike media depend on the elastic constants of both phases. It should be emphasized, however, that any attempt to apply these results in a quantitative sense to the problem of predicting conventional "moduli" or tensile strengths of rubber containing fillers is not justified for the following reasons. Derivations based on the mathematical theory of elasticity assume that the conditions of infinitesimal deformations, conformity with Hooke's law, and perfect elasticity are met. It is obvious that the usual deformations involved in the determination of tensile

properties, and the common occurrence of hysteresis and plastic flow, do not fall within the scope of the theory[19]. Furthermore, it was necessary, to obtain mathematical solutions, to assume that the elastic medium is rigidly bound to the surface of the particle, and that the latter is spherical. The assumption of rigid binding is certainly not true for all fillers, although it appears to be valid for carbon blacks and possibly for other fillers with outstanding reinforcing characteristics[20]. For technical mixtures composed of high concentrations of filler particles with resulting small distances of particle separation, the theoretical considerations are further complicated by particle interactions.

Photoelasticity studies carried out with a large disk of hard rubber cemented into a soft rubber sheet[21] show very good agreement between the observed stresses and those calculated[22] for the two-dimensional problem, and support the belief that the agreement for the three-dimensional problem would be equally good if it were possible to carry out the experiments for this case. Barnett[23] studied the stresses in a soft rubber sheet containing a large hard rubber inclusion by observing the distortion produced in a pattern marked on the sheet, and concluded that the stresses are greater at the surface of large particles than smaller ones. This conclusion is at variance with the results of the calculations given in this paper for spherical inclusions.

In addition to their bringing about photoelastic effects and pattern distortions, the stresses are revealed by their influence on the shape of the spots obtained in x-ray diffraction diagrams of rubber-filler systems. Gehman and Field[24] have made such measurements and found this to be the most satisfactory interpretation of their results. According to their explanation, the distortion of the lines of stress in the neighborhood of a particle results in a fiber axis making a varying angle with the direction of the applied tension, this orientation causing the x-ray spots to broaden into the observed arcs. Their observation that the crystallites are less perfectly aligned along the axis of stretch for channel black loadings as compared with other blacks of larger particle size may be attributable, according to the theory herein presented, either to the differences in the elastic constants of the different types of filler particles, or perhaps to different states of cure with resulting differences in the moduli of rigidity.

One would expect the stresses to vary with temperature; however, the magnitude of this effect cannot be estimated at present, since it would be required to know the temperature dependence of the elastic constants. Also, qualitative predictions are complicated by the fact that, while the bulk modulus and rigidity of the solid particle decrease with increasing temperature, the Young's modulus (or rigidity) of the natural or synthetic rubbers increases with temperature[25], and a compensating tendency may thus occur. Furthermore, at low temperatures crystallization in the rubber medium would also have to be considered; first, as modifying the average elastic constants of the medium, and second, as producing in effect further heterogeneity through the formation of crystallite "particles" imbedded in the otherwise amorphous medium.

SUMMARY

An attempt is made to develop a general theory of filler reënforcement by determining the stresses occurring in and about a spherical particle imbedded in a rubberlike medium subjected to an applied tension. For a system containing a single particle rigidly attached to the adjacent medium, an application of the theory of elasticity shows that, for infinitesimal deformations, the stress

components within the particle are independent of the radial distance from the origin, taken at the center of the particle. The stress components at a given point in the surrounding medium depend on the elastic constants both of the particle and of the medium, on the radius of the sphere, on the distance from the origin, and on the angle between the direction vector and the applied tension. Expressions are given for the average stresses in media containing many (independent) particles. Theoretical values of the bulk moduli of the synthetic rubbers considered in the treatment are derived from sound velocity data. Curves showing the spatial distribution of radial and shear stresses are presented for a range of values of elastic constants to be expected for different kinds of filler particles and rubberlike materials.

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REFERENCES

[1] Hock, in Memmler, "Science of Rubber", Reinhold Publishing Corp., New York **1934**, p. 495.
[2] Shepard, Street and Park, In "Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., **1937**, p. 380.
[3] Weiss, *Trans. Inst. Rubber Ind.* **18**, 32 (1942); RUBBER CHEM. TECH. **16**, 124 (1943).
[4] Hock, in Memmler, "Science of Rubber", Reinhold Publishing Corp., New York, **1934**, p. 495; Shepard, Street and Park, in "Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 380.
[5] Mott and Nabarro, *Proc. Phys. Soc. London* **52**, 86 (1940).
[6] Love, "Mathematical Theory of Elasticity", Cambridge Univ. Press, London, 4th Ed., **1927**, p. 141.
[7] Sezawa and Miyazaki, *J. Soc. Mech. Eng. Tokyo* **31**, 625 (1928).
[8] Richards, *J. Am. Chem. Soc.* **37**, 1643 (1915).
[9] Biscoe and Warren, *J. Applied Physics* **13**, 364 (1942).
[10] Smith, W. R., private communication.
[11] Landolt-Börnstein, "Physikalisch-chemische Tabellen", Verlag Berlin, **1935**, 3rd Supplement, I, p. 69.
[12] Adams and Gibson, *J. Washington Acad. Sci.* **20**, 213 (1930).
[13] Hencky, RUBBER CHEM. TECH. **6**, 217 (1933); Mooney, *J. Applied Physics* **11**, 582 (1940).
[14] Or, more strictly speaking, a spherical particle having the mean elastic properties of graphite.
[15] Rao, *J. Chem. Physics* **9**, 682 (1941).
[16] Lagemann and Corry, *J. Chem. Physics* **10**, 759 (1942).
[17] Bergmann ("Ultrasonics", Bell and Sons, Ltd., London, **1938**, p. 122) gives $V_s = 1275$ m. per sec. for acetonitrile at 28° C ($d = 0.775$). By means of Equation (8) and the known contributions (Reference 16) of the C—H and C—C bonds, we obtain a bond velocity of 284 for the —C≡N group.
[18] From the velocity of sound, one obtains the adiabatic compressibility by means of the relation: $V_s = (1/d\beta_{ad})^{0.5}$. The isothermal compressibility follows from the thermodynamic relationship: $\beta_{iso} = \beta_{ad} + \alpha^2 T/dc_p$, where α is the expansivity, T the absolute temperature, and c_p the specific heat at constant pressure. At ordinary temperatures, and for materials whose values of α and c_p are of the same order of magnitude as those of natural rubber, the second term is negligible.
[19] Nevertheless, one can by various practical techniques eliminate, or at least minimize, the latter two phenomena. It may be possible to treat the stress problem in the region where divergence from Hooke's law occurs by utilizing the theory of large deformations developed by Mooney, *J. Applied Physics* **11**, 5-2 (1940).
[20] Schippel, *Ind. Eng. Chem.* **12**, 33 (1920); Green, *Ind. Eng. Chem.* **13**, 1029 (1921); Boiry, *Rev. gén. caoutchouc* **3**, No. 24, 12; No. 25, 11 (1926); Depew and Easley, *Ind. Eng. Chem.* **26**, 1187 (1934).
[21] Thibodeau and Wood, *J. Research Natl. Bur. Standards* **20**, 393 (1938).
[22] Sezawa and Nishimura, *Rept. Aeronautical Research Inst. Tokyo Imp. Univ.* **6**, 25 (1931).
[23] Barnett, *Physics* **7**, 189 (1936).
[24] Gehman and Field, *Ind. Eng. Chem.* **32**, 1401 (1940).
[25] Anthony, Caston and Guth, *J. Phys. Chem.* **46**, 826 (1942); Peterson, Anthony and Guth, *Ind. Eng. Chem.* **34**, 1349 (1942).

FACTORS INFLUENCING THE PLASTICITY AND RECOVERY OF GR-S *

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One of the vital problems connected with the successful conversion from natural rubber to GR-S is the availability of the industry to mill and otherwise process this elastomer. When the polymer was first introduced, reports indicated at least twice as much equipment would be required to handle GR-S as to handle an equal volume of natural rubber. As the production of GR-S has increased, the product has become more uniform and less difficult to handle; it is now estimated that the processing of GR-S will not require more than 10 per cent more equipment than natural rubber.

In spite of this improvement the problem of processing GR-S is still important. One of the fundamental difficulties is due to the lack of correlation between laboratory tests and factory processability. Vila[1] showed that there is no relation between the Mooney plasticity and tubing speed, regardless of whether the basis is the plasticity of the compounded stock or of the uncompounded polymer used in the stock. Sturgis and Vincent[2] showed that there is no correlation between the milling characteristics of the raw polymer and plasticity, whether measured by Mooney plastometer, Williams parallel-plate plastometer, or the Williams pendulum plastometer. This apparent lack of correlation between plasticity and processability is difficult to understand. The present work was undertaken to determine whether a study of the changes which take place under various conditions of milling would give information that would explain this anomaly.

Except where otherwise specified, a single lot (source A) of GR-S was used throughout this work. All tests were carried out on 6 × 12 inch laboratory mills, with 600 grams of GR-S and a mill setting of 0.030 inch gauge. The temperature was followed by a thermocouple, and readings were made both on the back roll of the mill and in the GR-S itself. Samples were taken at the end of 3, 5, 10, 15, and 20 minutes of milling, and the plasticity was determined on a Williams parallel-plate plastometer. Plasticity is reported as the thickness, in thousandths of an inch, of a pellet after 3 minutes at 80° C, under a load of 5000 grams. The pellet has a volume of 2 cc. and an original thickness of 0.4 inch. Recovery is measured at room temperature 1 minute after removing the weight from the pellet, and is the difference in thousandths of an inch between the recovered thickness of the pellet and the plasticity number. All plasticity tests were made after the samples were allowed to condition at room temperature for 24 hours; preliminary work showed that this leads to the most uniform results.

In the first series of tests GR-S was milled under the following conditions: (*a*) as cool as possible—mill roll temperature 32° C (90° F) and maximum

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temperature in GR-S 43° C (110° F); (*b*) at intermediate temperatures—mill roll 70° C (158° F), maximum in GR-S 89° C (192° F); (*c*) at elevated temperatures—mill roll 121° C (250° F), maximum in GR-S 132° C (270° F). The results are given in Table I and Figure 1.

TABLE I

INFLUENCE OF MILLING TEMPERATURE ON MASTICATION OF GR-S WITHOUT CHEMICAL PLASTICIZER

Milling time (min.)	Williams Plasticity Recovery at Milling Temperature of:		
	32–43° C	70–89° C	121–132° C
0	128–45	128–45	128–45
3	122–47	131–52	142–96
5	124–37	130–69	138–130
10	123–26	131–127	132–180
15	119–42	123–50	126–149
20	111–13	117–33	105–20

The data show that, in the absence of a chemical plasticizer, GR-S breaks down most rapidly at low milling temperatures. In this respect it is similar to natural rubber. As the temperature of milling increases, surprising results appear in the recovery curve. Apparently the first effect of milling at high temperature is a marked increase in recovery. The maximum in the recovery *vs.* time of milling curve occurs after about 10-minute milling, and the magnitude of this maximum apparently increases as the temperature of milling increases. After 20-minutes of milling in this laboratory test, the effect has entirely disappeared and recovery shows a normal value.

Recovery has frequently been associated with gel formation, and it is possible that the first effect of increased temperature is to cause rapid gel formation. Further mechanical action finally breaks down the gel to a polymer with low recovery. If this is the true explanation, it may indicate the reason for a lack of correlation between plasticity recovery values and processability; the past history of the polymer in arriving at the measured value for the plasticity and recovery might well be expected to have a marked effect on the processability of the stock.

Since the results obtained in this series of tests were unexpected, the effect of high-temperature breakdown on a few additional samples of GR-S was investigated. The results are given in Table II. The recovery values for these samples after various milling periods are shown in Figure 2.

TABLE II

MILL MASTICATION OF THREE LOTS OF GR-S AT 121–132° C

Milling time (min.)	Plasticity Recovery of GR-S Samples		
	Mooney 85	Source B	Source C
0	185–133	131–61	138–61
3	166–88	129–33	154–90
5	165–108	124–36	142–77
10	161–138	120–49	137–62
15	158–166	108–15	128–34
20	154–128	97–7	127–31

The data show that the marked increase in recovery on short milling at high temperatures is characteristic of GR-S. The absolute value of the maximum and its position on the recovery-time of milling curve is, however, dependent

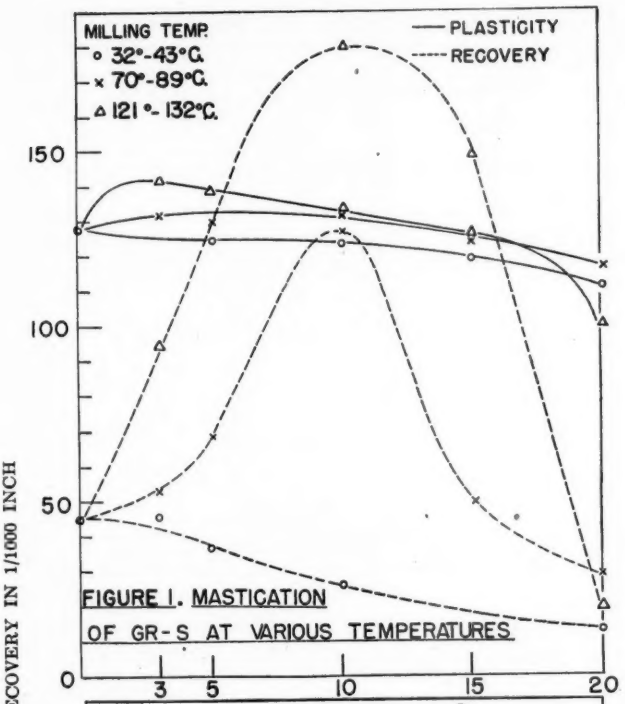

FIGURE 1. MASTICATION OF GR-S AT VARIOUS TEMPERATURES

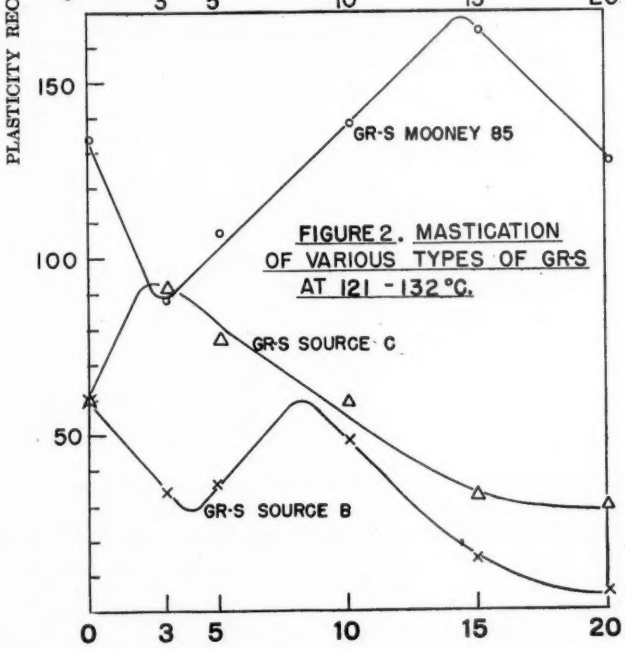

FIGURE 2. MASTICATION OF VARIOUS TYPES OF GR-S AT 121 - 132 °C.

on the particular lot of GR-S tested. With the sample of GR-S of high viscosity (85 Mooney) and the sample from source B, the first effect of milling is a decrease in recovery. Following this decrease, the recovery values increase with increased milling, pass through a maximum, and finally decrease as the time of milling is prolonged.

EFFECT OF CHEMICAL PLASTICIZERS

Sturgis and Vincent[2] developed chemical agents which markedly improve the milling characteristics of GR-S. The first series of experiments was therefore repeated with 2 per cent of agent RPA No. 5 as peptizer. (See Table III and Figure 3.)

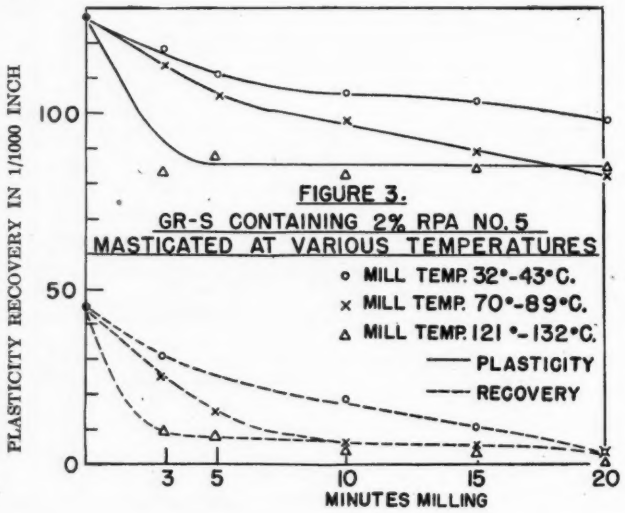

TABLE III

INFLUENCE OF MILLING TEMPERATURE ON WILLIAMS PLASTICITY RECOVERY OF GR-S CONTAINING 2% RPA NO. 5

Milling time (min.)	Plasticity Recovery at Milling Temperature of: 32–43° C	70–89° C	121–132° C
0	128–45	128–45	128–45
3	119–31	113–25	84–9
5	112–18	105–16	88–8
00	107–18	98–97	83–5
15	104–11	89–8	85–5
20	98–3	82–3	85–2

The results obtained in the presence of a chemical plasticizer are entirely different from those in its absence. The speed of breakdown, as measured by plasticity, is markedly increased by increasing temperatures of milling. In this respect the results are similar to those obtained when natural rubber is broken down in the presence of chemical plasticizers. In contrast to the results obtained in the absence of RPA No. 5, the recovery figures show a constant decrease throughout the milling operation, regardless of the milling temperature of GR-S. In fact, just as with the plasticity determination, recovery appears

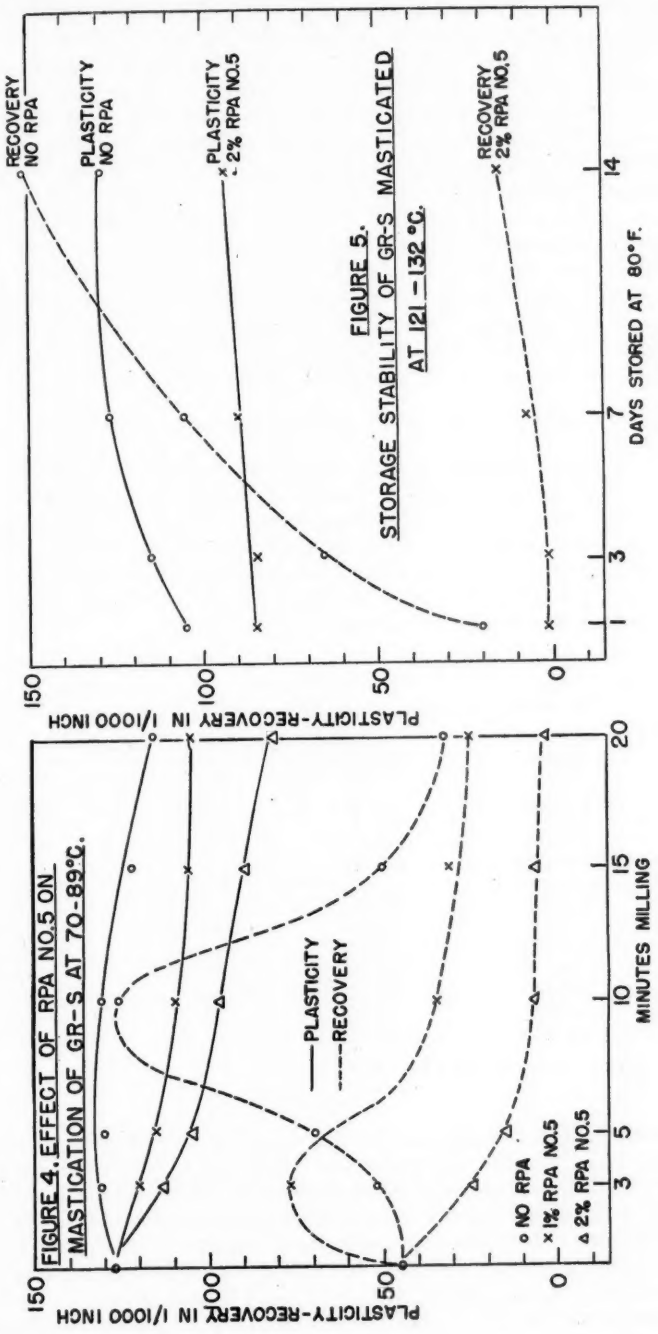
FIGURE 4. EFFECT OF RPA NO.5 ON MASTICATION OF GR-S AT 70-89°C.
PLASTICITY-RECOVERY IN 1/1000 INCH
150
100
50
0
PLASTICITY
RECOVERY
o NO RPA
× 1% RPA NO.5
Δ 2% RPA NO.5
3
5
10
15
20
MINUTES MILLING
FIGURE 5.
STORAGE STABILITY OF GR-S MASTICATED AT 121-132 °C.
RECOVERY NO RPA
PLASTICITY NO RPA
PLASTICITY 2% RPA NO.5
RECOVERY 2% RPA NO.5
1
3
7
14
DAYS STORED AT 80°F.

to fall off more rapidly, the higher the temperature at which GR-S is broken down. It is also noteworthy that, judged either by plasticity or recovery, the extent of breakdown, even at the conclusion of the milling operation, is much greater in the presence of the chemical plasticizer than in its absence.

In view of these surprising differences, it seemed important to determine the minimum concentration of the chemical plasticizer required to produce this effect. In this work the intermediate temperature of milling was selected, and the test was run at a mill roll temperature of 70° C (158° F) and a maximum temperature in GR-S of 89° C (192° F). The results are plotted in Figure 4. Under these conditions of milling, between 1 and 2 per cent of RPA No. 5 is required to remove the maximum in the recovery *vs.* time of milling curve. When only 1 per cent of the agent is employed, the maximum is still apparent, although it is shifted toward the left and is markedly decreased in magnitude. Undoubtedly the amount of RPA No. 5 required to eliminate the maximum depends both on the lot of GR-S used and on the milling temperature.

EFFECT OF STORAGE AFTER MILLING

Since the results obtained in this study had indicated a lack of thermal stability of GR-S in the absence of chemical plasticizer, the effect of varying times of storage after milling was investigated. The samples selected were those that had been milled for 20 minutes in the earlier set of experiments. Plasticity pellets were stored at a constant temperature of 26.7° C (80° F) in the dark, and plasticity recovery measurements were made after varying storage periods. The results are given in Tglde IV.

TABLE IV

PLASTICITY RECOVERY CHANGES OF MASTICATED GR-S[a] STORED AT 26.7° C

Per cent of RPA No. 5	Storage period	Plasticity Recovery at Milling Temperature of:		
		32–43° C	70–89° C	121–132° C
0	24 hours[b]	111–13	117–33	105–20
	3 days	107–7	118–117	115–66
	1 week	118–18	118–22	122–106
	2 weeks	131–21	120–30	124–52
1	24 hours[b]	112–21	105–26	108–46
	3 days	114–12	110–23	113–40
	1 week	115–16	111–20	117–42
	2 weeks	111–15	114–22	129–96
2	24 hours[b]	98–3	82–3	85–2
	3 days	97–5	81–2	85–1
	1 week	94–4	81–2	91–8
	2 weeks	96–7	81–2	94–15

[a] Plasticity recovery of unmasticated GR-S, 128–45.
[b] Original values.

The results for GR-S which had been broken down at the highest temperature—mill roll 121° C (250° F), maximum GR-S 132° C (270° F)—are plotted in Figure 5. GR-S, broken down in the absence of a chemical plasticizer, tends to revert to a condition resembling its original unmilled state on storage at room temperature. This effect is the more pronounced, the higher the temperature at which the GR-S is broken down, and is particularly apparent in the increased recovery of samples on storage at room temperature.

When masticated at 121° C, GR-S had a recovery 2 days after milling equal to the recovery of the original unmilled polymer; this change was still pro-

gressing after 2-weeks of storage, at which time the recovery was three times that of the original unmilled polymer.

GR-S, broken down in the presence of a chemical plasticizing agent, does not show this effect. When the test was discontinued after 2-weeks of storage at room temperature, the GR-S broken down in the presence of 2 per cent of RPA No. 5 at low and intermediate temperatures was in essentially the same condition, judged by either plasticity or recovery, as it was immediately after milling; GR-S broken down at elevated temperatures showed a small decrease in plasticity and a small increase in recovery.

REFERENCES

[1] Vila, "Plasticization and processing of GR-S", paper presented before the Division of Rubber Chemistry at its meeting in New York, October 5–7, 1943.
[2] Sturgis and Vincent, "Processability of GR-S and its improvement by chemical means", paper presented before the Division of Rubber Chemistry at its meeting in New York, October 5–7, 1943.

PROCESSING BEHAVIOR OF HIGH POLYMERS

CORRELATION WITH ELASTIC-PLASTIC PROPERTIES *

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The difficulties in correlating the processing behavior of synthetic high polymers with results obtained by standard plasticity methods[1] indicate that present methods do not completely evaluate polymer differences. A connecting knowledge between processing qualities and molecular structure would be of increasing value, not only as an aid to process control, but also as a possible guide to polymerization research. Observations on the elastic-plastic properties of high polymers seem to indicate some molecular differences that govern processing behavior. Williams[2] stated that, if one grade of rubber is considered, elastic strain is a function of resistance to flow. When different types of rubber or other materials are considered, the relation between plasticity and elastic strain does not remain constant. The purpose of this paper is to present some of the factors involved in carrying on further study of the plasticity, processing, and molecular structure correlation.

FACTORS INVOLVED IN PLASTICITY MEASUREMENTS

The high polymers considered here belong to that class of substances which exhibit, at ordinary temperatures, the phenomenon of high elasticity. As Simha[3] pointed out, Maxwell's approach to the elastic-plastic properties has been enlarged by many investigators. This theory of relaxation would be operative under two sets of conditions. First, a system under constant deformation would gradually lose potential energy equivalent to a decrease in internal stress, and second, in a system under constant external stress, the deformation would continue with time in order to compensate for the relaxation of internal stress.

Deformation of High Polymers.—The treatment of the high elastic phenomenon has been extensively studied under the second condition—constant external stress. Aleksandrov and Luzurkin[4] postulated that the total elastic deformation, D, would be equal to the sum of ordinary elastic deformation D_{OE} and high elastic deformation D_{HE} for a rubberlike substance. For unvulcanized polymers and plastics Tuckett[5] added a third term, the irreversible deformation due to viscous flow, D_{VISC}. The complete equation for total deformation would be the sum of these three terms:

$$D_{Total} = D_{OE} + D_{HE} + D_{VISC}$$

D_{OE} is the instantaneous deformation; that is, it occurs at very rapid rates of applied stress. Because the usual rates of deformation of processing equipment would never approach such instantneous rates, this term may be omitted.

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D_{HE}, high elastic deformation, reaches a limiting value or static state with respect to time at constant temperature as shown by Tuckett[6]. At constant loading time, D_{HE} reaches a limiting value with respect to temperature. The range of time and temperature in which high elastic deformation is operative depends upon the orientation time of the polymer molecules which, in turn, depends on molecular structure[7]. Standard processing equipment may operate in the range of temperature and deformation rate wherein high elastic deformation is a predominant factor for the high polymers discussed.

D_{VISC}, viscous deformation, increases linearly with time at a rate proportional to stress[8]; and at constant rate as temperature is increased, D_{VISC} increases directly. For any given type of high polymer, as noted by Flory[9] and Kauzmann and Eyring[10], viscosity or viscous deformation varies with molecular weight; and as molecular weight increases, the temperature for viscous flow is increased. On the other hand, high elastic deformation, which is more dependent on molecular structure, remains essentially in the same temperature limits as molecular weight varies. Tuckett[6] showed graphically how the relation of elastic deformation to viscous flow varies with molecular weight as the temperature changes; therefore it is advisable to select conditions for plasticity tests to correlate with processing behavior where viscous deformation is not predominant over high elastic deformation when a wide range of molecular weight is possible.

These theoretical considerations concerning variations in conditions for plasticity determinations were used as a guide in studying the processing behavior of polymers. In addition, all measurements, in agreement with Hoekstra[11], were made at a constant magnitude of deformation.

Plasticity and Elasticity at Rapid Rates to Constant Deformation.—As stated previously, the high elastic phenomenon is observed by relaxation of internal stress at constant deformation or with increasing deformation under conditions of constant external load. Since most processing equipment deforms high polymers at a constant rate and at a predetermined magnitude of deformation, the elastic-plastic properties of the polymers were compared under these conditions. The same theoretical principles that have been discussed for constant external load should be valid for constant deformation, for in either case a measure of internal stress is obtained. With constant load, internal stress relaxation is measured by a time-deformation function, and with constant deformation internal stress relaxation would be measured by a force, F, required to deform the polymer at any given rate (a force-time function).

This force-time function is shown experimentally in the right-hand section of Figure 1 at three different temperatures for one Butyl polymer. A cylindrical slug of Butyl rubber, 0.5 inch high and 0.75 inch in diameter, was compressed to a height of 0.25 inch. When the force in kilograms is plotted against the logarithm of time of compression, it appears as a linear function below a time of approximately 80 seconds at 25° C; above this time the line curves upward, an indication of increasing viscous deformation. As the temperature is increased, the point where the curve is no longer linear occurs at shorter and shorter times of compression.

If internal stress is the fundamental property measured, the work of Aleksandrov and Lazurkin[4] and Tuckett[6] can be transferred to a force-time function. As shown, within proper limits of time and temperature, force F appears as a linear function of the logarithm of time to deform the polymer to a given deformation:

$$F \propto \log t$$

The recovery after deformation, which is indicative of the internal stress remaining after a given deformation rate, should also be linearly related to the logarithm of time. As the left-hand graph of Figure 1 shows, the recovery-time of compression curves follow this general pattern within established limits of time and temperature.

Disadvantages of Standard Plasticity Methods.—In the case of masticated natural rubber, the standard methods of plasticity measurement satisfactorily predicted processing characteristics. If these same methods are applied to the processing behavior of a wide variety of synthetic polymers, certain limitations seem evident, and appear to be substantiated by poor correlation.

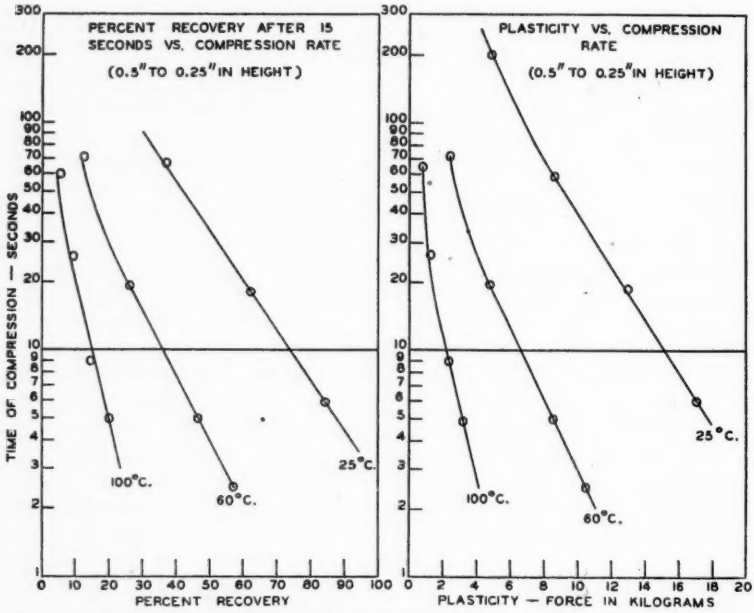


FIG. 1.—Elasticity and plasticity at various temperatures as a function of deformation rate.

As stated before, increased time of deformation results in increased or even predominant viscous deformation. This would be the particular disadvantage of the Williams plasticity measurements[12] with the usual deformation time of about 3 minutes. In the case of Butyl type polymers tested at higher temperatures, this long deformation time results in so much viscous flow that the elasticity or recovery effects are almost obliterated. In the case of Perbunan, with a much higher thermoelasticity in the unvulcanized state than Butyl, differences in the elastic qualities of the polymers upon 3-minute deformation are minimized.

The Mooney viscometer[13], on the other hand, does use rapid rates of shear, and as a viscometer, it may be utilized over a limited molecular weight range. However, when a wide variety of molecular weights and molecular weight distributions are encountered, this type of instrument does not accurately predict processing behavior. This fact is attributed to the wide differences in the elastic-plastic properties of polymers over such a range and to the relative

variations of these properties with temperature, for no provision is made in the Mooney method to evaluate elasticity. Of the many plastometers designed for natural rubber, the pendulum plastometer described by Williams[2] is notable because fairly rapid rates of compression to a constant thickness are used. Provision is made for measuring recovery or elasticity at a predetermined time; however, time of compression is a variable dependent on the stock stiffness. Hoekstra[14] also described a plastometer with compression rates in the neighborhood of 15 seconds under conditions of constant external load; no provision was made for an elastic strain measurement.

ELASTIC–PLASTIC PROPERTIES OF BUTYL

Figure 1 shows elasticity and plasticity at various temperatures as a function of deformation rate, for only one polymer. If many polymers are to be compared and their properties correlated with processing behavior, these comparisons should be made at a constant deformation rate so as to duplicate the conditions under which most processing equipment would operate. A constant compression rate of 10 seconds was selected for a twofold reason. At 25° C and 10 seconds, the deformation is predominantly high elastic for Butyl polymers. Also, time of deformation could be determined within about 0.5 second; therefore it appeared inadvisable to make polymer comparisons below this rate.

Elasticity and Plasticity as Functions of Temperature.—If the recovery and plasticity of the 10-second compression rate are obtained from graphs similar to Figure 1 and plotted against temperature, thermoelastic and thermoplastic curves for a variety of Butyl type polymers may be compared. In Figure 2 these curves are characterized by different slopes and positions which will reflect their processing behaviors. As the right-hand graph shows, the over-all general plasticity decreases as the polymer numbers go from 1 through 6. Polymer 5 has a slope somewhat different from the regular trend, which indicates different thermoplastic and thermoelastic properties. Although polymer 7 has high over-all plasticity, it is far less thermoplastic than any of the others.

These differences are reflected and accentuated in the thermoelastic curves on the left-hand graph of Figure 2. Polymers 1 through 6 show the same general slope as the elasticity curves, with polymer 5 again deviating a little from the general trend. This indicates that polymer 5 is less thermoplastic and more thermoelastic; a comparison of polymers 4 and 5 shows that their elastic properties at 100° C are more divergent than their plastic properties. The greatest difference in thermoelasticity appears for polymer 7; by plasticity standards it appears easy to process, but the thermoelastic curve predicts the reverse to be true.

The dotted curves show the behavior of natural rubber (smoked sheet) at two different states of breakdown. The upper dotted curves for both elasticity and plasticity represent smoked sheet after a 2-minute breakdown; the lower dotted curves represent the elastic-plastic properties after 20-minute mastication. Samples (200 grams) were milled on a 6 × 12 inch mill set at 0.030 inch at 158–160° F. Since about 20 minutes were required to mix completely a 200-gram rubber tread stock, the 20-minute breakdown was an attempt to approximate the state of breakdown of a compounded rubber polymer. These curves are notable because of their similarity to the thermoelastic and thermoplastic trend of Butyl polymers; butadiene polymers, such as Buna-N types, generally possess very different thermoelastic properties.

Factory Experience.—Judging from the slopes of the curves in Figure 2, two broad classes of Butyl type polymers appear. The first is represented by polymers 1 through 6; the second is represented by polymer 7. Experience with factory processing has shown that, in general, the first class (1 through 6) can be satisfactorily handled if Mooney viscosities are in the range 40 to 55.

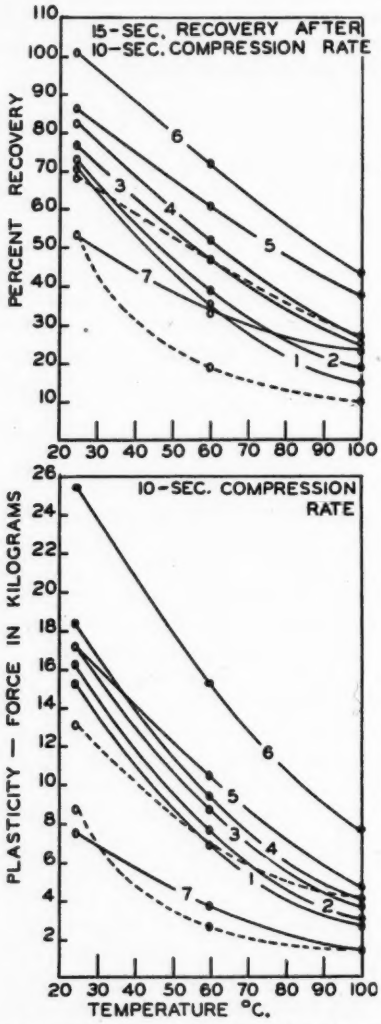


FIG. 2.—Elasticity and plasticity as functions of temperature for Butyl type polymers.

Even in this plasticity range, a polymer will sometimes exhibit anomalous behavior. When the Mooney viscosity of the first class of polymers rises much above the 55 limit, factory processing becomes difficult.

In the second class, represented by polymer 7, limited factory experience has indicated that Mooney viscosities cannot rise above 30 before processing

difficulties are encountered. In addition the processability of this type of polymer, as measured by extrusions, is not improved with increased tubing temperature; some reports indicate poorer behavior and appearance as forming temperatures are increased.

From the standpoint of product control, Mooney viscosity measurements are applicable over a limited molecular-weight range for a given class of Butyl polymers. When a different class of polymers or an anomalous processing behavior is encountered, the resulting differences in thermoelastic and thermoplastic relations require a change in viscosity standards or a more encompassing measurement of polymer properties. This is graphically explained by Figure 3.

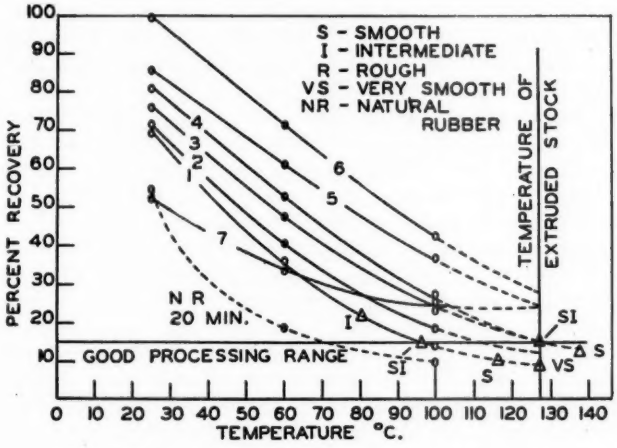


FIG. 3.—Thermoelasticity as a processing index for Butyl rubber.

Polymer No.	Mooney test (100° C)	Appearance	% Recovery at 100° C
1	42	VS	14
2	45	S	19
3	48	SI	24
4	54	SI	25
5	52	I	36
6	75	R	42
7	38	I-R	25
N.R.	...	VS	10

Thermoelasticity as Processing Index for Butyl.—The temperature-recovery curves of Figure 2 are shown in Figure 3, with dotted line extrapolations to the higher extrusion temperatures. The table under Figure 3 shows that Mooney viscosity values remain in line with the appearance ratings of extruded stocks only for polymers 1, 2, 3, 4, and 6. For polymers 5 and 7 the other consideration of elasticity, especially thermoelasticity, is needed. The recovery data at 100° C (Figure 3) do compare fairly well with the appearances of extruded stocks. However, the thermoelasticity curves must be consulted for a complete picture of elasticity and processing behavior.

In the comparisons of extrusion and elasticity, the various Butyl polymers were compounded with 50 parts of an easy-processing channel black in a tread type of stock. Extrusions were carried out with a constant stock temperature of 258–260° F, controlled by a needle pyrometer. Test stocks without sulfur or accelerator were used.

To obtain some basis for rating polymers, a tentative elasticity limit for good processing behavior was established. On the basis of both thermoelasticity and thermoplasticity, polymer 1 is the most processable, and the appearance of extruded specimens at 260° F stock temperature is very smooth. If tread compounds of polymer 1 are extruded at lower and lower temperatures, shown by the triangles on curve 1 (Figure 3), the appearance of the extruded specimen becomes less smooth as conditions progress up the thermoelastic curve. In other words, as temperature is decreased, elasticity is increased, and the appearance of the extruded stock is similar to a higher-molecular-weight, more elastic polymer. At the point about 95° C for the stock temperature, the appearance begins to appear slightly rough. This point corresponds to an elasticity of 15 per cent recovery, and is set up as a tentative elastic limit for good processing. Therefore all the thermoelastic curves or their extrapolations should meet this processing limit line before 127° C (stock extrusion temperature) is reached. Polymers 1, 2, 3, and 4 meet this specification, whereas others, such as anomalous polymers 7 and 5, do not approach the limit. Polymers 3 and 4 just meet the processing line at the extrusion stock temperature, although their elastic properties originate from slightly different positions at lower temperatures. If the temperature of the extruded stock with polymer 3 is increased, the appearance of the extruded specimen appears smoother, as the thermoelastic curve on Figure 3 shows. This is additional evidence of the dependence of extrusion quality on thermoelasticity.

These differences in thermoelastic behavior can be explained by molecular differences in the polymers. Sample 7 contains small amounts of gel or insoluble polymer, in addition to considerable quantities of low-molecular-weight polymers. Since there is no gel polymer in sample 5, its slightly anomalous behavior can be attributed solely to molecular weight distribution.

The dotted thermoelastic line again represents natural rubber after a 20-minute mastication under the conditions noted previously. This thermoelastic curve intersects the tentative Butyl rubber elasticity limit well below maximum extrusion temperatures, and reflects the excellent processing behavior of masticated natural rubber.

Effect of Molecular Weight Distribution.—A series of polymers varying in molecular weight distribution, but maintaining constant weight-average molecular weight, was made up by mixing portions of low-molecular-weight polymers on a mill with various high-molecular-weight polymers so that the weight average was 35,000. Polymer 1 was used as the control, and the calculated molecular weights were checked analytically by the Staudinger viscosity method. They are given in the table under Figure 4, along with a two-member series at a molecular weight level of 45,000. The accompanying Mooney values are of interest since they show that wide variations in molecular weight distribution would lead to erroneous processing predictions.

Thermoelastic and Thermoplastic Behavior.—The solid curves of Figure 4 show how the molecular weight distribution affects the thermoelastic and thermoplastic properties of a Butyl rubber of similar weight-average molecular weight. As molecular weight-distribution is widened for a given weight—average molecular weight—the polymer becomes more thermoelastic and less thermoplastic. A wide distribution of molecular weight results in a greater overall plastic product, but the increase in thermoelasticity indicates a poorer processing polymer. The same results with the polymers of 45,000 molecular weight are shown by dotted lines. Polymer 3 is just on the processing border line; that is, its extrapolated thermoelastic curve just reaches the 15 per cent

recovery line at 127° C. Polymer C, of wider molecular weight distribution, possesses a flatter thermoelastic curve which, on extrapolation, would be unable to meet the low elastic standard.

Relation of Extrudability to Molecular Weight Distribution.—The thermoelastic and thermoplastic properties of the various molecular—weight distributions are directly related to the swelling of the extruded specimens. In the previous section more emphasis was given to elasticity than to plasticity.

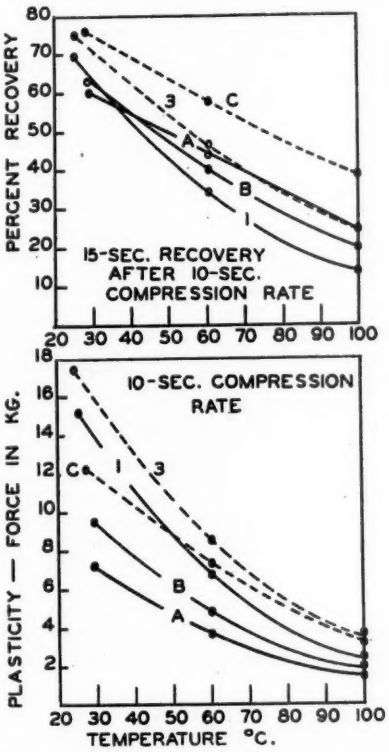
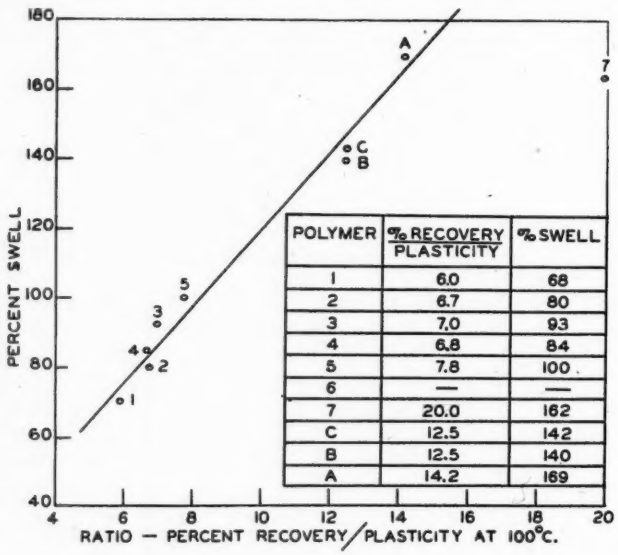


FIG. 4.—Effect of molecular weight distribution on thermoelastic and thermoplastic properties of Butyl rubber.

Polymer No.	Mol. wt. distribution	Calcd. mol. wt.	Mol. wt. by analysis	Mooney test
1	Normal	...	35,000	42
B	Wider	35,000	36,000	32
A	Widest	35,000	33,000	26
3	Normal	...	45,000	48
C	Wider	45,000	...	45

Plasticity, however, is an important consideration, and must be used in conjunction with recovery to predict accurately the processing and molecular characteristics of Butyl polymers. Although the thermoelastic or recovery-temperature curves can indicate the appearance of an extruded stock, the ratio of recovery to plasticity indicates molecular weight distribution which, in turn, governs the amount of swell a polymer yields after a definite processing deformation.

In the table accompanying Figure 5, the ratios of recovery to plasticity are shown for a group of Butyl polymers, along with corresponding swell data. The swell of a compounded tread type of stock is plotted against the ratio of recovery to plasticity at 100° C for the raw polymer. Polymers A, B, and C, with increasing molecular weight distribution, are compared to regularly prepared polymers; all but polymer number 7 lie close to a straight line. This indicates that a difference in molecular weight distribution between regularly prepared polymers (such as 1, 2, 3, 4, and 5) does exist, for they follow the same swell-elastic-plastic relation as polymers A, B, and C. Polymer 5, which in earlier discussions showed some slight deviation from regular thermoelastic behavior, appears farther up the line in the region of greater swell, and consequently suggests the presence of a greater molecular weight distribution. Polymer 7 lies away from the line, presumably because of the presence of gel in the polymer, which would undoubtedly alter the relation based solely on molecular weight distribution.



POLYMER	% RECOVERY / PLASTICITY	% SWELL
1	6.0	68
2	6.7	80
3	7.0	93
4	6.8	84
5	7.8	100
6	—	—
7	20.0	162
C	12.5	142
B	12.5	140
A	14.2	169

FIG. 5.—Relation of extrusion swell to the ratio elasticity/plasticity.

PERBUNAN TYPE POLYMERS

Unlike Butyl rubber, Perbunan type of polymers are plasticized by mill mastication, although the degree of breakdown is not so severe as that possible with natural rubber. Processing qualities of Perbunan differ from those of natural rubber in a manner reflected by thermoelastic properties. Even after drastic mill mastication, Perbunan is very thermoelastic, and the variations in the degree of thermoelasticity in conjunction with plasticity govern mill behavior.

Thermoelastic and Thermoplastic Differences.—The elastic-plastic properties of a series of raw unmasticated Perbunan polymers are shown in Figure 6. The tremendous difference between the thermoelastic properties of these poly-

mers and of Butyl types is evident. Elasticity increases with increasing temperature in all cases. This upward trend, as noted by Treloar[16], is indicative of actual primary-bond cross linkage. The behavior of raw unmasticated

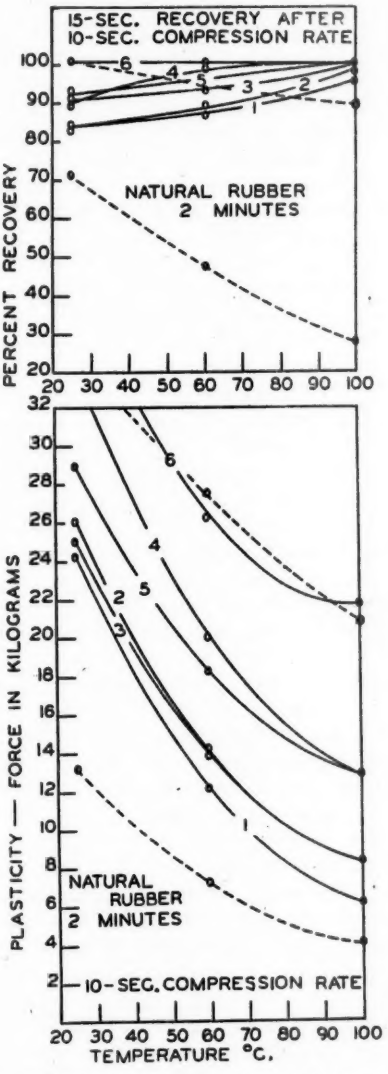


FIG. 6.—Elasticity and plasticity as functions of temperature for unmasticated Perbunan type polymers.

rubber (upper dotted line) is somewhat different from these Perbunan type polymers, as shown by the descending elasticity curve. This descending curve also seems to substantiate Treloar's view[15] that the strength and gel of raw rubber are due in greater part to mechanical entanglement of the molecules

and possible van der Waals forces. The behavior of a 2-minute laboratory-masticated natural rubber is also shown in comparison. The plasticities of these raw polymers cover a wide range, but in some instances the values cannot be considered indicative of processing qualities.

When these Perbunan type polymers are subjected to laboratory mastication, they remain relatively more elastic at high temperatures when compared to Butyl or natural rubber types. This behavior is noted in Figure 7, where actually the thermoelastic differences between the polymers are more diversified than in the case of the raw polymers. For comparison the dotted lines again refer to natural rubber at two stages of mill breakdown. The laboratory breakdown procedure for these polymers (admittedly drastic) consists of continuously milling 50 grams of polymer for 5 minutes on a 6 × 12 inch mill set at 0.007 inch; the roll temperatures are maintained at 115° ± 5° F.

The thermoelastic curves of the masticated polymers vary widely from polymer 1, with a decreasing slope, to polymers 4 and 5, with increasing slopes. Polymers 2 and 3 lie in intermediate positions. Polymer 6 is unique; although its thermoelastic curve has a higher overall level, its decreasing slope is similar to polymer 2 or 1. This behavior is interesting in view of the low plasticity, as noted in the right-hand graph of Figure 7. The thermoplasticity curves do not show the general wide divergence of the thermoelastic curves. They all descend steeply as the temperature is increased, which seems fundamentally different from the natural rubber curves. Although exhibiting a steeper temperature-plasticity function than natural rubber over the temperature range studied, the Perbunan types exhibit thermoelastic behaviors of a generally flat nature. For masticated natural rubber (dotted lines) and most Butyl type polymers, the thermoelastic and thermoplastic properties show similar downward trends.

Correlation of Processing Behavior with Elastic-Plastic Properties.—Critical processing factors may not be the same for all types of polymers; the respective cases of Butyls and Perbunans are examples. Butyl rubber is changed only slightly by ordinary milling, so the critical processing factor for these polymers is their behavior toward forming or extrusion after compounding. The Perbunan type, on the other hand, is altered by milling, and is usually premasticated before addition of compounding ingredients. This mill behavior during mastication is the more critical processing factor, and for this reason mill behavior is correlated with elastic-plastic properties.

Laboratory Correlation.—Milling behavior was determined by banding time, on a 6 × 12 inch mill set at 0.030-inch clearance with roll temperatures maintained at 115° ± 5° F. The end point was considered to be the time in minutes when 250 grams of polymer formed a continuous band about the slow roll, free from holes in the center portion of the band. These determinations were made for five Perbunan types (Figure 7). Williams plasticity values, obtained with a 10-kg. weight at 80° C for a 3-minute compression time, are shown, along with corresponding Mooney viscosity data. The Williams data were obtained on laboratory-masticated samples. Mooney determinations were run on the raw polymer at 100° C; the Mooney reading recorded was obtained after a 20-minute continuous run. Recovery and plasticity at 100° C were obtained from the curves, and are tabulated in the form of a ratio (Figure 7).

The banding time seems to correlate well with the recovery values for polymers 1, 2, 4, and 5. The same may be said for the Williams plasticity values, which are, respectively, deformation and recovery in thousandths of an inch. In the case of polymer 1 (lower molecular weight) the Williams recovery

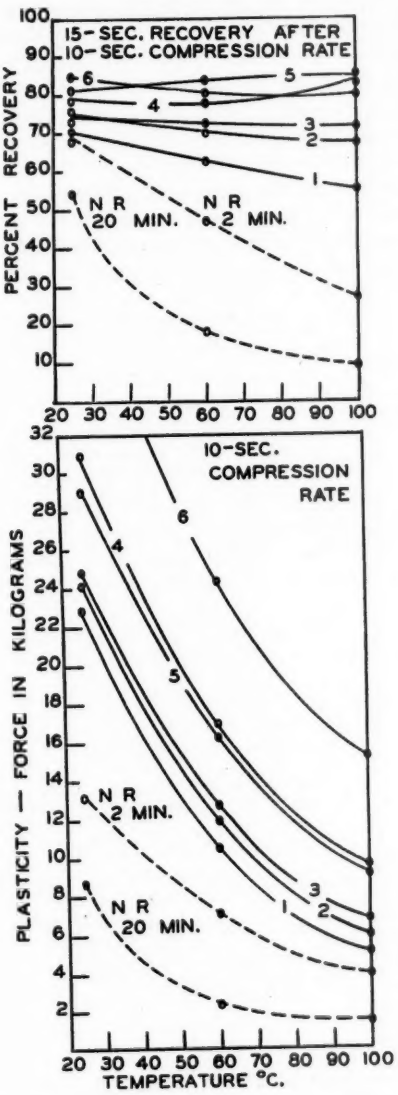


FIG. 7.—Elasticity and plasticity as functions of temperature for Perbunan polymers after laboratory breakdown.

Polymer No.	% Recovery-plasticity at 100° C	Band. time, sec.	Williams plasticity	20-Min. Mooney test
1	55– 5.2	14	102– 4	70
2	68– 6.0	18	120–16	90
3	71– 6.8	...	135–22	94
4	84– 9.8	26	148–44	136
5	84– 9.2	30	140–49	138
6	79–15.0	13	151–58	175

value at this slow Williams compression rate has been minimized out of proportion to the others. Mooney plasticity values for the four polymers also yield rough correlation. Polymer 6 represents an anomalous case that cannot be explained by these plasticity standards. Polymer 6 has a lower banding time than the others, although it has the lowest plasticity (highest plasticity reading). Polymer 6 also has an intermediate recovery at 100° C; some elasticities of these Perbunan types are higher, some are lower. The polymers 4 and 5, which require long banding times, do not show a downward trend to the thermoelastic curves of the masticated polymers. This is the one instance where the properties of polymer 6 are not anomalous with mill behavior, for this least plastic of the polymers does exhibit a downward sloping thermoelastic

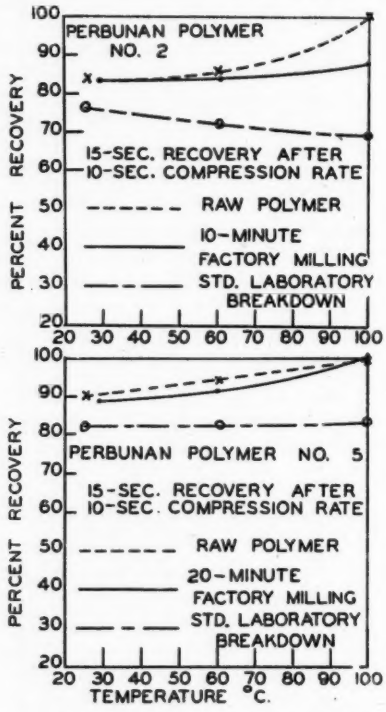


FIG. 8.—Comparison of factory and laboratory degrees of breakdown.

curve. These considerations lead to the conclusion that a relation of recovery to plasticity is important. Polymer 6 has a lower ratio of recovery to plasticity than that of the other Perbunan types. From the standpoint of milling, it appears that film strength of the banded polymer, which is related to molecular weight and to plasticity, dictates the amount or degree of elasticity a stock can tolerate before it fails to band properly. In other words, it may be postulated that a polymer of greater film strength can tolerate greater elasticity and still maintain comparable milling behavior. These factors of film strength, elasticity, and processability seem to depend, as noted in the case of Butyl polymers, on molecular weight distributions, in conjunction with average molecular weight.

Factory Correlation.—Only two types, polymers 2 and 5, have been followed in a factory mixing; as shown by their elastic-plastic properties, they represent a rather wide range of processing behavior. On factory mastication, polymer 2 required 10 minutes to form a satisfactory band, whereas polymer 5 required 20 minutes. The condition of the band with polymer 5 after 20-minute milling was still not so good as polymer 2; it was characterized by small holes throughout.

The thermoelastic curves of Figure 8 indicate an explanation for the mill behaviors and conditions of the mill band after the respective 10- and 20-minute millings for polymers 2 and 5. The solid lines give the thermoelastic properties of the polymer after samples were removed from the factory mill at the end of the mastication period. Polymer 2 is characterized by an 88 per cent recovery at 100° C; polymer 5 has 100 per cent recovery at 100° C. At the state of factory breakdown, polymer 2 is less thermoelastic than 5. The dotted lines represent the thermoelastic properties of the original polymers; judging by the differences between the solid and dotted curves, it is evident that factory mastication has a greater breakdown effect on polymer 2. This is possibly due to the relative "tightness", as well as amount of original gel content.

The dot-dash curves represent thermoelastic properties of polymers 2 and 5 after standard laboratory breakdown; factory breakdown does not approach this degree of laboratory breakdown. The curves for laboratory mastication show that polymer 2 possesses a better temperature elastic behavior, which may reflect better molecular weight distribution, in addition to higher over-all plasticity.

REFERENCES

[1] Sturgis and Vincent, "Processability of GR-S and its improvement by chemical means", paper presented before the Division of Rubber Chemistry at its meeting in New York, October 5–7, 1943; Vila, "Plasticization and processing of GR-S", paper presented before the Division of Rubber Chemistry at its meeting in New York, October 5–7, 1943.
[2] Williams, *Ind. Eng. Chem. Anal. Ed.* **8**, 304 (1936).
[3] Simha, *J. Applied Physics* **13**, 201 (1942).
[4] Aleksandrov and Lazurkin, *Acta Physicochim. U.S.S.R.* **12**, 647 (1940).
[5] Tuckett, *Chem. & Ind.* **62**, 430 (1943).
[6] Tuckett, *Trans. Faraday Soc.* **39**, 158 (1943).
[7] Tuckett, *Trans. Faraday Soc.* **38**, 310 (1942); **39**, 158 (1943).
[8] Tuckett, *Chem. & Ind.* **62**, 430 (1943); *Trans. Faraday Soc.* **39**, 158 (1943).
[9] Flory, *J. Am. Chem. Soc.* **62**, 1057 (1940).
[10] Kauzmann and Eyring, *J. Am. Chem. Soc.* **62**, 3113 (1940).
[11] Hoekstra, *Chem. Weekblad* **31**, 754 (1934); RUBBER CHEM. TECH. **9**, 55 (1936).
[12] Williams, *Ind. Eng. Chem.* **16**, 352 (1924).
[13] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).
[14] Hoekstra, *Proc. Rubber Tech. Conf. London*, 1938, p. 362; RUBBER CHEM. TECH. **12**, 434 (1939).
[15] Treloar, *Trans. Faraday Soc.* **36**, 538 (1940); RUBBER CHEM. TECH. **13**, 795 (1940).

VULCANIZATION OF BUNA-S (GR-S) WITH ORGANIC SULFUR COMPOUNDS

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INTRODUCTION

Standard tests designed for rubber[1] have shown that free-sulfur vulcanizates of Buna-S (butadiene-styrene copolymer) are more resistant to oxidation than rubber. In early work with Buna-S, Street and Ebert[2] used the oxygen bomb test as a means of showing this advantage of Buna-S over rubber. Later studies of Neal and Ottenhoff[3] on the aging of GR-S vulcanizates showed that the air-pressure test, which is run at a relatively high temperature, is more severe than the oxygen-bomb test. Although many laboratory methods of measuring the physical properties of copolymer vulcanizates have failed to be indicative of performance in actual service, two tests have been developed which have been generally accepted as at least indicative of the properties necessary for satisfactory performance. The first of these tests is the change in

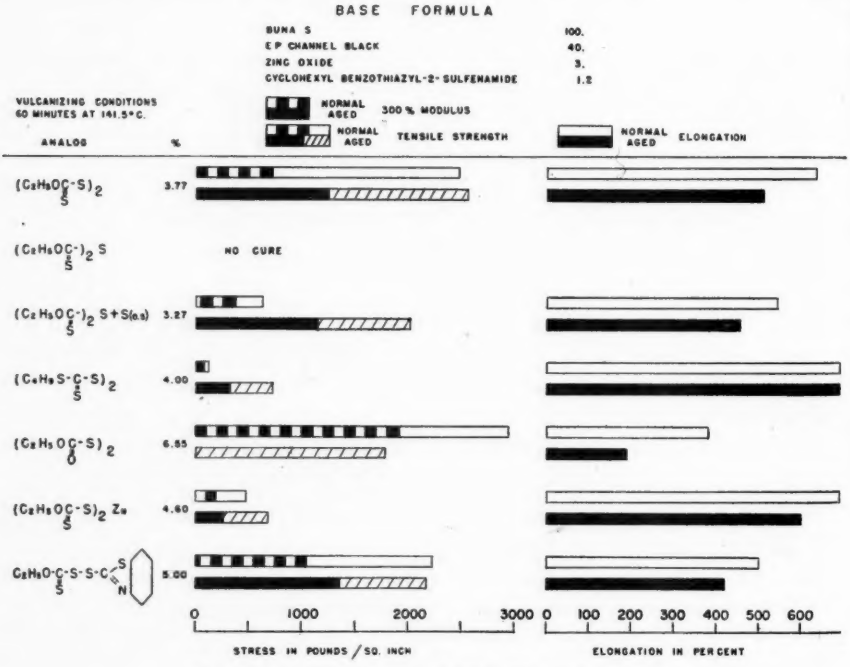


FIG. 1.—Vulcanizing activity of ROC—SS—COR analogs.
‖ ‖
S S

stress-strain properties after subjecting the vulcanizate to circulating air at 100° C for 24 and 48 hours; the second test is the rate of growth of slits in the vulcanized specimen during either tension or compression bending. Recent data of Prettyman[4] have shown good correlation of flex-cracking with road tests.

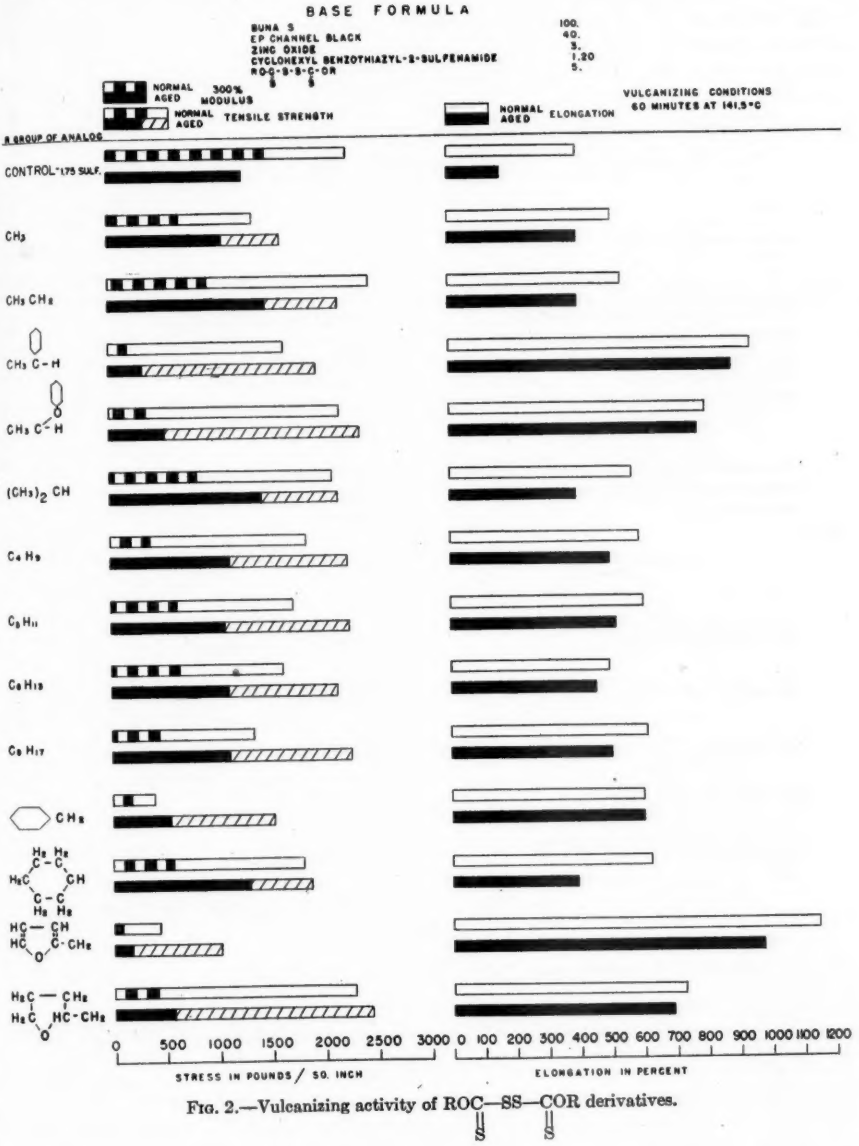


FIG. 2.—Vulcanizing activity of ROC—SS—COR derivatives.

Much research has been published[5] on free-sulfur vulcanization for improving resistance to heat and to flex-cracking, but this has been essentially a study of accelerator-activator variables. The sulfur variable has been a compromise

in relation to acceleration of either high hysteresis loss or poor heat resistance. The influence of the solubility of free sulfur has been studied by Williams[6], who found that good dispersion could be obtained only by masterbatching at a temperature above the melting point of sulfur, and then cooling rapidly. Replacement of sulfur used for vulcanization has been mentioned by Vila, who obtained excellent stress-strain properties with tetramethylthiuram disulfide in concentrations up to 3 per cent. No heat-resistance data were given, however. Sturgis, Baum and Vincent have presented data on vulcanization with dinitrobenzene, which show a marked superiority of this agent over free sulfur in imparting resistance to heat embrittlement.

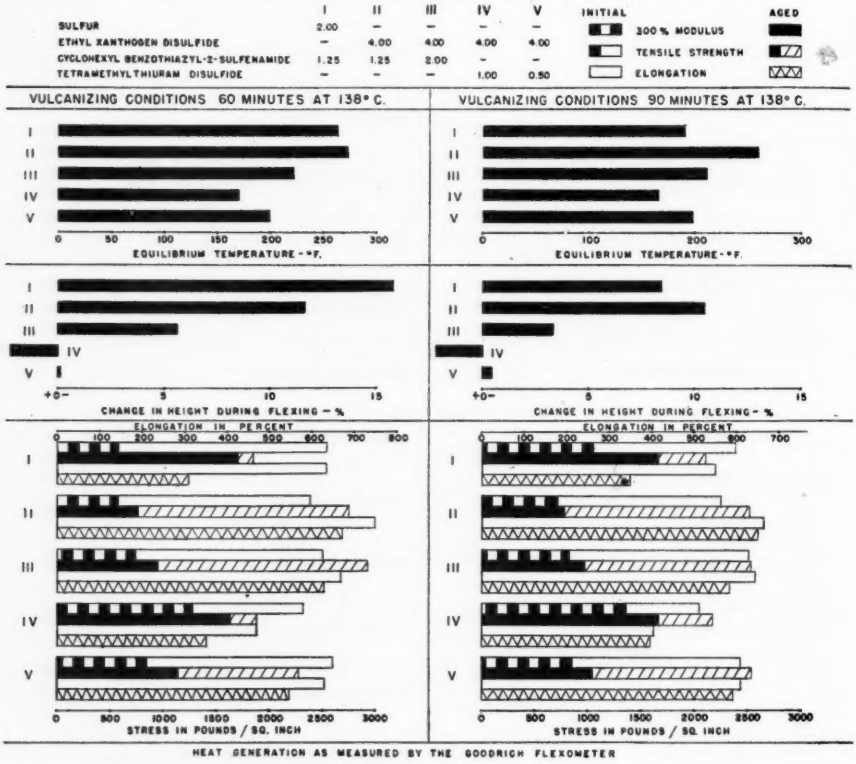

BASE FORMULA - 100. BUNA S, 45. EP CHANNEL BLACK, 3. ZINC OXIDE, 7. SOFTENER
I II III IV V
SULFUR 2.00 – – – –
ETHYL XANTHOGEN DISULFIDE – 4.00 4.00 4.00 4.00
CYCLOHEXYL BENZOTHIAZYL-2-SULFENAMIDE 1.25 1.25 2.00 – –
TETRAMETHYLTHIURAM DISULFIDE – – – 1.00 0.50
INITIAL
AGED
300 % MODULUS
TENSILE STRENGTH
ELONGATION
VULCANIZING CONDITIONS 60 MINUTES AT 138° C.
VULCANIZING CONDITIONS 90 MINUTES AT 138° C.
EQUILIBRIUM TEMPERATURE - °F.
CHANGE IN HEIGHT DURING FLEXING - %
ELONGATION IN PERCENT
STRESS IN POUNDS / SQ. INCH
HEAT GENERATION AS MEASURED BY THE GOODRICH FLEXOMETER

FIG. 3.

The present studies on vulcanization show the superior physical properties which are obtained with organic sulfur compounds in place of free sulfur.

In addition to the data shown in Figures 1 to 5, other results have indicated that alkylxanthogen tetrasulfides with activators and accelerators are too slow in vulcanizing activity to be of industrial application. Morpholine and piperidine tetrasulfides vulcanized well, but the vulcanizates had very poor resistance to tearing and to heat. Studies with tetramethylthiuram disulfide confirmed the results of Vila[7], but this and other thiuram polysulfides were found to impart poor flex-cracking resistance at elevated temperatures. Car-

bamyl and other amine sulfides vulcanize Buna-S to give vulcanizates of excellent heat resistance, but are deficient in good hysteresis properties.

Among the most readily prepared xanthogen disulfides are those from the xanthates of the corresponding monohydric alcohols. Xanthates cannot be

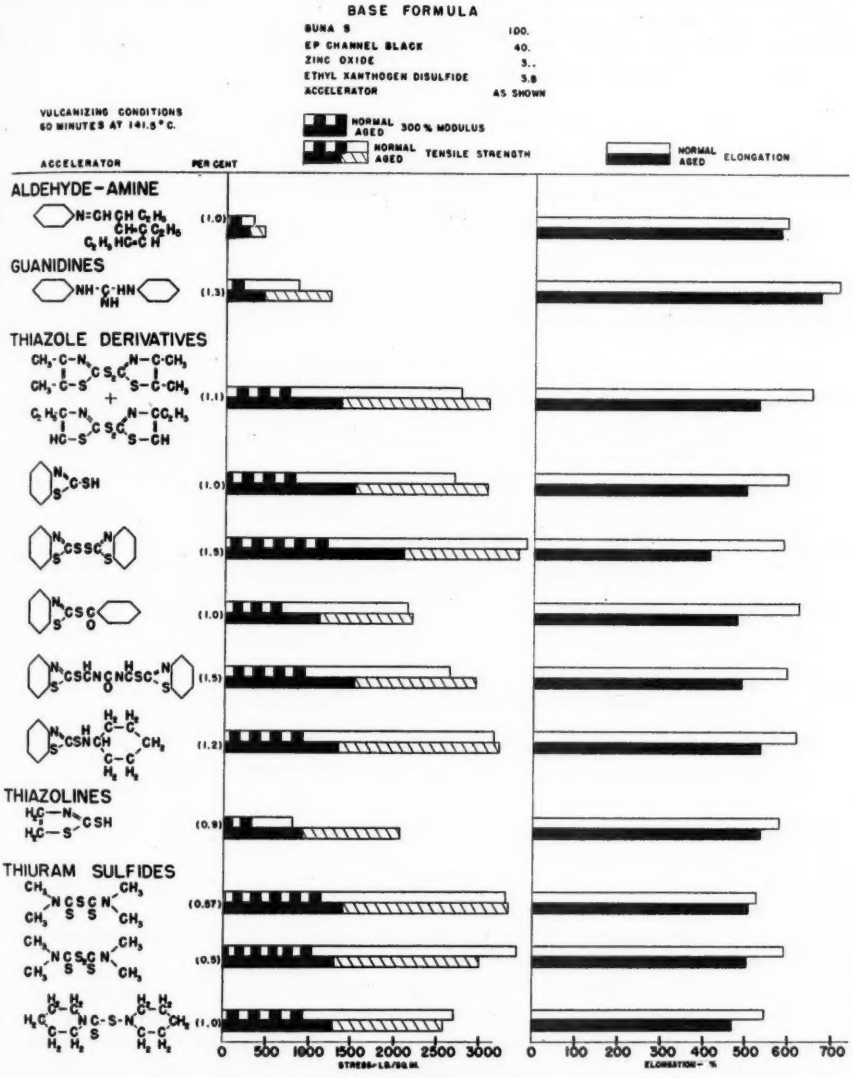


FIG. 4.—Effect of accelerator variation with ethyl xanthogen disulfide.

made from polyhydric alcohols in satisfactory yields when the hydroxyl groups are on adjacent carbon atoms, but polyxanthogen disulfides can be prepared from polyhydric alcohols such as diethyleneglycol. Phenolic compounds do not yield xanthates.

Although Cadwell[9] first observed the use of xanthogen disulfides as accelerators of the vulcanization of rubber, it was recently found in this laboratory that vulcanizates of Buna-S using alkylxanthogen disulfides as vulcanizing agents in conjunction with accelerators were decidedly superior to vulcanizates of free sulfur in heat, and flex-cracking resistance. More specifically, these studies also show an application of ethylxanthogen disulfide to vulcanize Buna-S although similar improvements in properties were obtained with butadiene-acrylonitrile copolymers and natural rubber.

EXPERIMENTAL PROCEDURE

Processing.—Compounds were mixed in a 6″ × 12″ open mill according to normal processing practice. All batches were allowed to rest at least 16

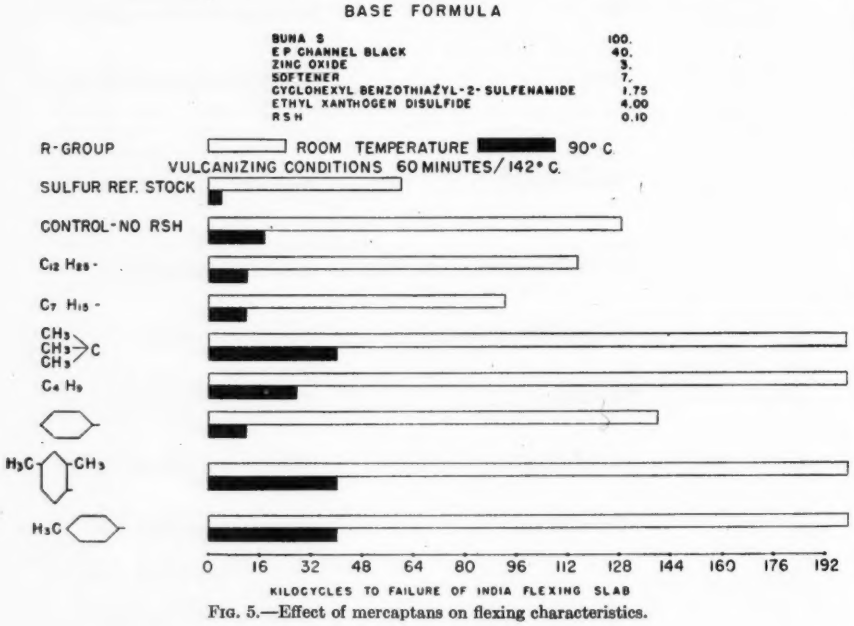


FIG. 5.—Effect of mercaptans on flexing characteristics.

hours after mixing, were then resheeted to the desired gauge, and were vulcanized in a press as soon as possible.

Stress-strain properties.—The vulcanizates were evaluated on a Scott machine according to ASTM procedures[10].

Flex-cracking.—The rate of growth of a 3/32″ slit cut in the center of a standard India flexing specimen[11] was measured in 64ths inch until failure. The speed of the rotor was approximately 10 cycles per second. An atmosphere of air at 90° C was provided by means of resistance heaters within an insulated cover over the entire rotating mechanism. Air was sufficiently circulated by the fanning action of the specimens on the periphery of the wheel to assure an even temperature throughout the enclosure.

Hysteresis.—Hysteresis or heat buildup under compression was measured in a standard Goodrich flexometer[12], using a stress of 175 pounds per square inch and a stroke of 0.175 inch. The temperature was recorded at 5-minute

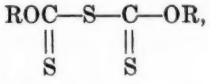
intervals for 30 minutes. The percentage static compression and percentage change in height during flexure also were measured.

Heat resistance.—Resistance to heat was noted by the change in stress-strain properties after subjecting the vulcanizates to circulating air at 100° C for 24 hours.

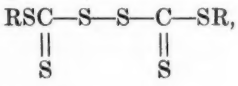
Static fatigue failure under strain.—Standard tensile specimens were clamped in a suitable rack and stretched to 250 and 400 per cent strain. The time to failure was observed either at room temperature or at 60° C.

DISCUSSION [13]

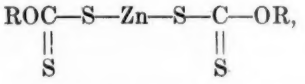
Analogs.—Figure 1 shows the vulcanizing activities of several analogs of ethylxanthogen disulfide. These data show that the monosulfide,



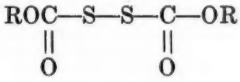
the oxidized trithiocarbonate,



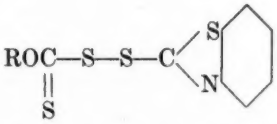
and the zinc salt,



effected little vulcanization, whereas the carbethoxy disulfide,



gave excellent initial stress-strain properties but poor heat resistance. The mixed disulfide,



gave results most comparable to ethylxanthogen disulfide. The relative degrees of vulcanizing activity of the various alkyl or cyclic derivatives of ethylxanthogen disulfide compared with sulfur are shown in Figure 2. It is evident that, from the compounds shown in Figures 1 and 2, an —S—S— linkage is essential to vulcanization, because neither the monosulfide nor the zinc salt of the disulfide exhibit any appreciable vulcanization. The function of the R group is considered somewhat secondary from results of the mixed disulfide and the alkyl derivatives of ethylxanthogen disulfide. The poor results of the methyl derivative may be attributable to the fact that it is the first member of the series. Other things being equal, ethylxanthogen disulfide was selected for further study because of availability of cheap raw materials, ease of preparation and high yield.

Acceleration.—With Buna-S, maximum results were obtained with 3.77 to 4.0 per cent of ethylxanthogen disulfide (3.77 per cent is equivalent to 2.0 per

cent total sulfur). While acceptable stress-strain properties were obtained with normal amounts of mercaptobenzothiazole derivatives (1.0–1.5 per cent), the best hysteresis characteristics as measured by the Goodrich flexometer, as well as excellent stress-strain properties, were obtained with higher percentages (Figure 3). Tetramethylthiuram disulfide and *N*-cyclohexylbenzothiazyl-2-sulfenamide were found to develop best all-round properties as shown in comparison with other type accelerators in Figure 4. With tetramethylthiuram disulfide, faster vulcanization than with normal sulfur-accelerator (mercaptobenzothiazole type) ratio was obtained.

Activation.—Zinc oxide was the only effective metallic-oxide activator found. The diphenylguanidine salts of phthalic acid, phosphoric acid, *o*-phenolsulfonic acid, and pentachlorophenol showed no activation. The effect of addition of organic acids was slight.

Effect of thiols.—The effect of adding alkyl- and arylthiols in proportions of 0.05–0.50 per cent to the mill mixes in increasing flex-cracking resistance at elevated temperatures is shown in Figure 5. Studies in this range indicated optimum results at 0.10 per cent, with no significant improvement noted with higher proportions. These data, taken at room temperature and 90° C, show clearly the marked influence of minute amounts of *t*-butyl-, xylyl-, and *p*-methylphenylthiols in increasing the flex life of the vulcanizates.

Static fatigue failure under strain.—D. E. Reynolds[14] of the Central Research Laboratories, Monsanto Chemical Company, Dayton, Ohio, observed premature failure of sulfur-vulcanized Buna-S while under tensile strain during exposure to x-rays. This observation led to the test described. It is not known what significance may be ascribed to such a test, but it seems reasonable that these observations, which show that ethylxanthogen disulfide vulcanizates lasted several hours longer, may have some bearing on the poor resistance to tread-cracking of tires under strain.

CONCLUSIONS

1. Buna-S has been vulcanized by a number of organic sulfur compounds, most interesting of which are alkylxanthogen disulfides.

2. The optimum results were obtained with a stock containing 4.00 per of ethylxanthogen disulfide, with either 2.00 per cent of *N*-cyclohexylbenzothiazyl-2-sulfenamide or 0.50 per cent of tetramethylthiuram disulfide.

3. The effect of small additions of *t*-butyl-, xylyl-, and *p*-methylphenylthiols was a pronounced improvement in the flex-cracking resistance of a vulcanizate containing ethylxanthogen disulfide.

These observations suggest the industrial application of ethylxanthogen disulfide to alleviate some of the serious deficiencies so characteristic of Buna-S vulcanizates.

REFERENCES

[1] American Society for Testing Materials, Standards on Rubber Products D 572–40 (1940).
[2] Street and Ebert, RUBBER CHEM. TECH. **14**, 211 (1941).
[3] Neal and Ottenhoff, *Ind. Eng. Chem.* **36**, 352 (1944).
[4] Prettyman, *Ind. Eng. Chem.* **36**, 29 (1944).
[5] Carlton and Reinhold, *Rubber Age* (N.Y.) **52**, 29 (1942); Vila, *Ind. Eng. Chem.* **36**, 1469 (1942); Neal, *Rubber Age* (N.Y.) **53**, 31 (1943); Juve and Garvey, *Ind. Eng. Chem.* **36**, 215 (1944).
[6] Williams, *India Rubber World* **108**, 35 (1943).
[7] Vila, *Ind. Eng. Chem.* **34**, 1269 (1942).
[8] Sturgis, Baum and Vincent, *Ind. Eng. Chem.* **36**, 348 (1944).
[9] Cadwell, U. S. patent 1,532,225.
[10] American Society for Testing Materials, Standards on Rubber Products D412–41 (1941).
[11] Torrance and Peterson, *India Rubber World* **80**, 62 (1929).
[12] Lessig, *Ind. Eng. Chem. Anal. Ed.* **9**, 582 (1937).
[13] It should be noted that these data were obtained with Buna-S (GR-S) made in February–June 1943, and consequently the results are somewhat poorer than have been obtained more recently.
[14] Reynolds, D. E., private communication.

DERIVATIVES OF SYNTHETIC RUBBER *

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For more than a century the chemistry of the rubber hydrocarbon has attracted the attention of chemists from both a theoretical and practical standpoint. During this time a large number of rubber derivatives other than reaction products with sulfur have been studied. To the early chemist these derivatives were of interest primarily as a means of obtaining further information concerning the structure of the rubber molecule. The abundant supply and low price of natural rubber during the late nineteen twenties greatly stimulated interest in its use as a chemical raw material, and resulted in the commercial development of a number of these derivatives.

By processes of cyclization, chlorination, and hydrochlorination, natural rubber was converted into products with great hardness and rigidity, and increased resistance to moisture and corrosive influences. These products found many uses in protective coatings of the paint and lacquer type, in wire-insulation compositions, as films for packaging foods and other products, as paper coatings to reduce moisture penetration, as adhesives, and in a number of other applications. A résumé of the technological development and uses of these derivatives and of their synthetic facsimiles is presented below.

CYCLIZED RUBBER

As early as 1910, Harries[1] recorded the preparation of an isomer of the cycle type by treating Para rubber at ordinary temperatures with concentrated sulfuric acid. The product was an amorphous powder, insoluble in the usual rubber solvents, and appreciably more saturated than ordinary Para rubber. Ostromislensky[2] in 1915 and Kirchhof[3] in 1920 also investigated the reaction products with sulfuric acid. But it was not until 1927 that Fisher's investigations led to the production of commercially useful thermoplastics from a rubber derivative.

The purpose of Fisher's research[4] was to convert rubber into the thermoplastic products with properties similar to gutta-percha, balata and shellac. He accomplished this by heating in sheet form a mixture of rubber with approximately 10 per cent of its weight of either an organic sulfonyl chloride or an organic sulfonic acid. A mixture of 7.5 parts of *p*-phenolsulfonic acid and 100 parts of rubber gives a flexible guttalike, benzene-soluble product, having the properties shown in Table I.

This is a very good rubber-to-metal adhesive, and has been used extensively for this purpose. These sulfuric-acid type conversion products can be vulcanized to nonthermoplastic materials by heating with sulfur and, since they are chemically less unsaturated than rubber, they do not require so much sulfur.

Another type of cyclized rubber is formed by the reaction of halogenated acids of tin, such as chlorostannic acid or chlorostannous acid, on rubber[5].

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TABLE I

PROPERTIES OF CYCLIZED RUBBER

(*p-Phenolsulfonic acid reaction product*)

Specific gravity	0.980
Tensile strength	2600 lbs. per sq. in.
Elongation at break	27 per cent.
Impact strength	50 lbs. per sq. in.
Dielectric strength	47,500 volts per mm.

The reaction may be accomplished by direct addition of approximately 10 per cent of the reagent to rubber on a mill or to a solution of rubber in benzene[6]. The products contain a certain proportion of bound chlorine, depending on the temperature of the reaction and other conditions. In carrying out the solution process, which is the preferred procedure, a 10 per cent solution of rubber in benzene is heated with chlorostannic acid in a jacketed reactor equipped with a reflux condenser. An enormous reduction in the viscosity of the solution takes place during the heating, and the rubber is converted into a thermoplastic resin.

The physical properties of the product are determined by the time of reaction, and a series of resins can be obtained having distortion points varying from 25° to 110° C. The resin is recovered from the solvent as a finely divided powder, and vacuum dried. The solubility of this product can be increased and its solution viscosity reduced by milling between rolls. The milled material is soluble in aliphatic, aromatic, chlorinated and terpene hydrocarbons, and films deposited from these solutions are colorless, transparent, glossy, nontacky and heat-sealing.

The cyclized rubber derivatives made by this process can be made to vary from balatalike substances to exceedingly hard materials resembling ebonite, depending on the time of reaction. They are amber colored thermoplastics which are definitely more saturated than rubber, having a polycyclic ring structure. The material having a softening point of 80° to 100° C has the optimum mechanical properties, and the figures in Table II are presented to

TABLE II

PROPERTIES OF CYCLIZED RUBBER

(*Chlorostannic acid reaction product*)

Rubber hydrocarbon content	92 per cent minimum
Specific gravity	1.06
Softening point	80°–100° C
Cold flow (2000 lbs. per sq. in., 120° F., 24 hrs.)	0.00035 in./in.
Moulding temperature	125°–155° C
Tensile strength	4000–5000 lbs. per sq. in.
Compressive strength	8500–11000 lbs. per sq. in.
Flexural strength	7000–9000 lbs. per sq. in.
Water absorption (24 hrs'. immersion)	0.03 per cent

illustrate its dissimilarity to unvulcanized rubber, which has practically the same rubber hydrocarbon content.

These cyclized derivatives possess remarkable resistance to acids, alkalis and other corrosive influences and have, therefore, found application in paints to resist these conditions. For this purpose a derivative having a softening point of 55° to 65° C is preferred. This material is an excellent medium for dispersing pigments by plastic mixing, which is much more effective than the

conventional wet-grinding methods employed in the paint industry. Electron microscope studies of carbon blacks treated in this manner show very good dispersion of the pigment. When such mixtures of cyclized rubber derivative and pigments are mixed with a solvent, the derivative dissolves, releasing the pigments in a dispersed condition suitable for use in the formulation of protective coatings. Such coatings dry rapidly and then gradually oxidize to form hard films. The cyclized rubber will take up about 8 per cent of oxygen, and the oxidized film becomes insoluble in aliphatic hydrocarbons, but is still swollen, although not dissolved, by aromatic hydrocarbons. This hardening or oxidation process is accelerated by exposure to light, by baking, or by the use of paint driers.

As the 55° to 65° C softening point derivative can be handled in various solvents at fairly high concentration and dries to a transparent, colorless, glossy, nontacky film which is highly resistant to water and moisture vapor penetration, it has been used quite extensively as a coating for making paper both moistureproof and vaporproof. Where transparency is not a factor and some gloss and heat seal strength can be sacrificed, mixtures of this material with various waxes have been used, either as hot dips or coating solutions. Another use is as a stiffening agent for rubber in wire-insulation compounds which must be extruded to proper gauge with accurate centering and must have good physical, electrical, and water resisting characteristics.

A cyclization product with somewhat lower softening point has been used as a rubber-to-metal adhesive. Through its application and subsequent vulcanization, rubber is welded to metal with integral adhesion. A wide range of compounds may be bonded to steel, aluminum, zinc, lead, tin and wood in this manner.

CHLORINATED RUBBER

Another quite widely used rubber derivative is chlorinated rubber. One of the earliest records of the production of chlorinated rubber seems to be that of Engelhard and Day[7] in 1859. They described the products which they obtained as ranging from a flexible limp material like leather to a white hard mass of the consistency of vulcanite. Since that time numerous other investigations have been carried out both of a practical and theoretical nature.

A chlorinated rubber introduced by Peachey[8] more than twenty-five years ago, was the first derivative of this type to be used commercially. It was obtained by the exhaustive chlorination of natural rubber, and was characterized by its stability towards alkalies, acids, nitrous fumes and corrosive agents. It was described as a grayish-white amorphous powder that could be masticated, calendered like rubber, or moulded, with or without the addition of filling material, into any desired shape, by the combined action of gentle heat and pressure.

A possible explanation of the mechanism of the chlorination of rubber has been proposed by Kirchhof[9], according to which chlorine first adds on at the double bonds and after these have become saturated HCl is split off, leaving the product unsaturated. This is followed by addition of chlorine at the double bonds to form trichloro and tetrachloro derivatives, which contain 61.4 and 68.5 per cent chlorine, respectively. The commercial products contain 65 to 68 per cent chlorine, and thus correspond to mixtures of the trichloro and the tetrachloro derivatives.

Rubber chloride is a light yellow-to-white odorless solid, of specific gravity 1.5. It is unattacked by strong acids and alkalies, and although it is chemically inert, it is readily soluble in aromatic hydrocarbons and is compatible

with a large number of plasticizers and natural gums. Paints can be prepared from these solutions by the conventional wet-grinding procedures. The outstanding characteristic of such paints is their resistance to corrosive influences. Because of its high adhesion when properly compounded, rubber chloride may be used as an adhesive for wood, leather, paper, cork and cloth.

HYDROCHLORINATED RUBBER

As early as 1900, Weber[10] prepared rubber hydrochloride by passing hydrogen chloride through a solution of rubber in chloroform and precipitating the reaction product with alcohol. Weber and subsequent workers used the results of their investigation chiefly as a means for studying the chemical composition of rubber.

The addition of hydrogen chloride to rubber has been carried out commercially by three different processes. According to the first method, rubber in the form of small cubes is heated with liquid hydrogen chloride under pressure. The second method comprises passing gaseous hydrogen chloride into a solution of milled rubber until the theoretical quantity has been absorbed; then the mixture is allowed to ripen for a period, and the excess hydrogen chloride is neutralized. In the third method, thin sheets of milled rubber are suspended in gaseous hydrogen chloride until the desired quantity has been reacted.

The commercial grades of rubber hydrochloride made by the first method are thermoplastic, tough products which have good electrical properties and ozone resistance, and are available in the form of hard massed sheets. These products may be vulcanized with sulfur and accelerators to give rubberlike products which are no longer thermoplastic. The principal applications of these hydrochlorides are in paper coatings, protective coatings, electrical and other moulded products, adhesives and printing inks.

The rubber hydrochloride prepared according to the second method is used chiefly in the manufacture of transparent films for packaging foods and other products. By reacting rubber with hydrogen chloride, a product containing about 34 per cent chlorine is theoretically obtainable, having the formula $(C_5H_9Cl)_n$. The desired characteristics are obtained, however, by limiting the chlorine content to 28 to 30 per cent. Compounds which contain a greater chlorine content are brittle, while those with less chlorine are tacky. Coloring materials and an organic protective agent to prevent deterioration from the sun are added to the solution. The solution is then spread as a film on a moving belt, is dried, and then is continuously removed from the belt.

Actual packaging applications of rubber hydrochloride were begun in 1936. Since then there has been a rapidly increasing use of this material as a protective wrapper in the food industries for the packaging of cheese, meat, frozen and dehydrated foods, coffee, and other products. The unique properties of this rubber hydrochloride which make it particularly suitable for these applications are[11]:

1. Low moisture vapor transmission.
2. Heat-sealing qualities.
3. Oil, grease and solvent resistance.
4. Low-temperature flexibility.
5. Nonblocking at high temperatures.
6. High tear strength.
7. High shock resistance.
8. Gas diffusion characteristics.

The relatively poor sunlight resistance of this material is not of importance in these applications.

The physical properties of rubber hydrochloride may be fundamentally changed by a tensilizing treatment[12]. In this process the rubber hydrochloride sheet material is heated to 180 to 230° F to make it plastic. While in the plastic state the material is stretched from three to six times its original length, and then is cooled in the stretched condition. Compared with untreated material of the same gauge, the tensilized material has much greater tear resistance at right angles to the direction of stretch, and has greater tensile strength in the direction in which it was stretched.

SYNTHETIC RUBBER DERIVATIVES

In many instances the derivatives of natural rubber described above met a need which was not fulfilled by any other available materials and their commercial use was, therefore, firmly established when our supply of natural rubber was cut off by the war. Whether all of these needs can be met with derivatives of synthetic rubber is a subject for considerable research. Several such derivatives have been prepared and their properties studied, and the results obtained thus far indicate that many of the desirable features possessed by the derivatives of natural rubber can be duplicated in the synthetic products.

Due to the status of world affairs research on synthetic rubber derivatives has not advanced rapidly. However, some investigations have been carried out in the field of chlorinated and cyclized derivatives which are of considerable interest.

CHLORINATED SYNTHETIC RUBBERS

Several patents have been issued covering the preparation of chlorinated butadiene rubbers[13]. In one of these the inventor claims that derivatives with desirable lacquer producing properties are obtained by effecting the chlorination at a temperature above 60° C. The chlorination products which are obtained are said to have a higher chlorine content and a higher softening point than those prepared at a lower temperature. These products are also claimed to be compatible with drying oils such as linseed oil, whereas products which are obtainable by chlorination at lower temperature are insoluble in such oils.

To obtain a chlorinated synthetic rubber of a sufficiently low viscosity for the lacquer industry, another process describes subjecting the butadiene polymer to an oxidizing treatment at a temperature of 80° to 140° C in the presence of antioxidants. After chlorination, it is stabilized by incorporation of ethylene oxide derivatives. The chlorination product thus obtained has a relative viscosity of 10 in a 5 per cent solution in chloroform.

Another investigator[14] has found that the viscosity of synthetic rubber chloride depends on the conditions of chlorination, separation, drying and stabilization. The higher the degree of chlorination, the more stable and resistant is the product. The most effective solvents are benzene and chlorohydrocarbons, followed by esters and some ketones. Mixtures of solvents may, under some conditions, be more effective than pure solvents. The most viscous solutions are those in carbon tetrachloride. This investigator found that synthetic rubber chloride is miscible with oils, and resins, but not with crude rubber, cellulose esters, phenolformaldehyde resins, wax and paraffins. The greater the molecular weight, the better it forms films; the strength of the films depends on the chlorine content. The alkali resistance makes it suitable

for use in paints for concrete. However, because this synthetic rubber chloride absorbs light strongly, it is unsuitable as an outside lacquer. Furthermore, the elasticity and toughness of the films are greatly affected by temperature.

In Russia[15] synthetic rubber and rubber produced from native plants like kok-saghyz, Valochnik, and guayule, have been used as the bases for chlorinated rubber. Initial tests were made with rubber in a dry state as well as in solution, but all attempts at chlorinating dry rubbers ended in failure. Dichloroethane was found to be the best solvent for chlorination. Chlorination of the natural rubbers was accelerated by iodine, antimony chloride, and aluminum chloride. Chlorination in the presence of iodine increased the stability of chlorinated rubbers; aluminum chloride and antimony chloride increased the percentage of fixed chlorine. The resins in resinous rubbers for the most part chlorinate and eventually act as plasticizers.

Chlorination of synthetic rubbers in solutions containing iron reduced the stability and solubility of the product. Lead decreased the solubility but not the stability of the product. Both iron and lead had no effect on the amount of chlorine which combined.

As far as chlorine content and outward appearance are concerned, the closest resemblance to chlorinated plantation rubber was shown by kok-saghyz (55 per cent chlorine), Sovprene (59.5 per cent chlorine), and beresklet gutta-percha (58 per cent chlorine). Then came eukomia gutta-percha (54.7 per cent chlorine) and S.K.B. (52 per cent). Chlorinated kok-saghyz and S.K.B. showed the highest viscosity, so it was possible to prepare lacquers in xylene with concentrations of only 15 to 20 per cent. The other types of chlorinated rubber have much lower viscosity, and the concentration in xylene can be 30 to 40 per cent.

The stability of these chlorinated rubbers was not impaired by heating for 12 hours at 60 to 80° C, nor did any softening take place when the temperature was kept at 60° C, but with prolonged heating at 80° C, chlorinated S.K.B. begins to soften.

As a result of British investigations, butadieneacrylonitrile rubbers have also been chlorinated[16]. It has been shown that tough, strong, elastic products, which have an extensibility of the order of 600 per cent over the nonchlorinated starting material, can be obtained by controlling the degree of chlorination so that only up to 3 per cent of chlorine is contained in the polymer. The rubbery chlorinated product is sufficiently plastic to be worked on rubber rolls, and may be modified by the addition of fillers. It is claimed that these modified or unmodified products may then be substituted for the ordinary polymer in oil-resistant cable sheathing, moulding compounds, oil gaskets, tires, hose, or wherever a product having greater strength, toughness, or elasticity is required.

By the process of another invention[17] there is produced a white, thermally-resistant, thermoplastic chlorinated polyisobutylene polymer, having any desired percentage of chlorine, by chlorination under controlled temperature and pressure in the presence of discoloration-preventing substances. The desired amount of the stabilizer or discoloration preventor is added to the polymer solution before chlorination. The preventor may be an aminoacetic acid in the proportion of 0.05 to 5.0 per cent; or may be acetic acid or an amine, such as diamyl amine. Chlorination is carried out in a solvent such as carbon tetrachloride, hexachlorethane, etc.

The resulting polymer is highly resistant to heat, and retains the clear white color of the pure chlorinated polymer in the presence of traces of iron salts, which otherwise would produce serious discoloration and easy breakdown.

The exact method of operation of the discoloration-preventing substances is still unknown, but it is believed that the chlorine combines with the traces of metals present to produce metal chlorides, which may be the cause of the breakdown and discoloration, and that the preventor or stabilizer substances function by forming some type of compound with traces of iron, aluminum and zinc salts, which compounds are either insoluble or are removed from the sphere of chlorination by some other chemical factors.

Another white, heat-stable, chlorinated polysiobutylene polymer is described[18] which contains small proportions of chlorinated rubber substance. In practicing the invention, the polyisobutylene and natural rubber are dissolved in a chlorine-resisting solvent, and then chlorinated under controlled conditions of temperature and pressure. A product containing varying percentages of chlorine may be obtained.

In the lower ranges of chlorine content the resulting material is a plastic white solid and, in the very lowest ranges, is slightly sticky and stringy. The higher percentages of chlorine result in a substance which tends to be more or less friable, and even brittle. The product is described as particularly desirable for paints, lacquers, enamels and insulating materials, as well as for coating compositions generally in combination with both the natural resins and the synthetic resins, and also for printing inks, leather finishes, insulating varnish, etc.

The solubility of the chlorinated product varies according to the proportion of chlorine introduced, and with the solvent, the lower proportions of chlorine giving a material which is relatively highly soluble in hydrocarbons and chlorinated hydrocarbons; higher percentages of chlorine give a material which is soluble in some oxygenated solvents, and compatible with the ordinary drying oils and also with the natural and synthetic resins.

In our own laboratory we have chlorinated a variety of synthetic elastomers, and have obtained a material from GR-S synthetic rubber (75 per cent butadiene: 25 per cent styrene copolymer) which compares very favorably with the chlorinated natural product, as shown by the data in Table III.

TABLE III

PROPERTIES OF CHLORINATED GR-S

Chlorine content	53 per cent
Viscosity (20% solution in toluene)	0.50–20.0 poises
Solubility	Aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters of organic acids
Compatibility (5% or more)	Paraffin, chlorinated paraffins, tricresyl phosphate, dibutyl phthalate, isobutyl linoleate
Stability	Equal to chlorinated natural rubber
Softening point	75°–85° C
Moisture vapor transmission on glassine:	
Coating weight Lbs. per ream	M.V.T. Grams per sq. m. per 24 hrs.
3.3	114.7
5.6	70.4
10.5	49.9
Flexibility	Greater than chlorinated natural rubber
Specific Gravity	1.36–1.39
Adhesion	Equal to chlorinated natural rubber
Tensile strength	5100 lbs. per sq. in.
Elongation	18.7 per cent

In mechanical properties, this material is superior to chlorinated natural rubber, which at 67 per cent chlorine content has a tensile strength of 3450 lbs. per sq. in. and 12.5 per cent elongation. Preliminary tests on chemical resistance indicate that the synthetic product is equal to the natural. The superior flexibility of the synthetic material should open avenues of use which have been closed to chlorinated natural rubber.

CYCLIZED SYNTHETIC RUBBERS

Reference to cyclized synthetic rubber in the literature is practically nonexistent. Rubberlike polymers and copolymers undergo cyclization with various degrees of reluctance, giving products which vary from soft and rubbery to hard and brittle products, as described below.

Cyclized GR-S (butadiene: styrene)—Whereas natural rubber may be cyclized by treating a boiling benzene solution with a catalyst, such as chlorostannic acid, GR-S requires the much higher temperatures obtainable in such solvents as phenol, cresol, neutral coal tar oils and naphthalene. In general, the procedure consists of heating a 10 to 15 per cent solution of GR-S in one of the above solvents to a temperature of 160° to 180° C, and adding the proper amount of catalyst with agitation. After approximately 10 minutes the temperature begins to rise, and the viscosity of the solution increases to form a gel. The temperature then decreases and the viscosity is reduced until, after about 30 minutes, the reaction mixture becomes a thin brown-colored solution, from which the cyclized GR-S may be recovered by steam distillation or extraction of the solvent.

The resulting product is a brown resin which is soluble in aromatic and chlorinated hydrocarbons, but insoluble in aliphatic hydrocarbons and alcohol. If the reaction is stopped while in the gel stage, the product is insoluble in common organic solvents. The procedure is quite flexible, and changes in one condition can be compensated by changes in another.

For example, an increase in the amount of catalyst employed increases the rate of reaction and accomplishes the same result at a lower temperature. The hardness and softening point of the product depends on the time of reaction in much the same manner as in the case of natural rubber and can be varied from soft and rubbery to a hard and brittle resin, having a softening point of 105° C. Analogous to the natural rubber reaction, a product of desired softening point may be obtained by stopping the reaction at the proper viscosity.

Various cyclizing agents or catalysts have been studied, and chlorostannic acid, stannic chloride and boron trifluoride have been found to be effective in the solvents mentioned. None of these bring about a reaction in boiling toluene solutions of GR-S at atmospheric pressures, but insoluble gels have been obtained in sealed tubes at 160° C. Reactions in toluene may, however, be obtained using anhydrous aluminum chloride as the catalyst, with formation of a hard, high softening point, insoluble resin, but this appears to be the product of a Friedel and Crafts' reaction rather than a cyclization. By heating GR-S in 10 per cent solution in naphthalene with 15 per cent its weight of concentrated sulfuric acid for 3.5 hours at 180° C, a hard rubbery product was obtained. Hydrogen chloride does not produce a resinous product at 180° C as it does with natural rubber.

By following the procedure outlined above, cyclized derivatives of GR-S can be obtained, having the properties indicated in Table IV.

The low moisture-vapor transmission of this material suggests its use in moistureproof coatings for paper. Such coatings are clear and transparent,

TABLE IV

PROPERTIES OF CYCLIZED GR-S

Specific gravity	0.99–1.03
Softening point	55°–105° C
Solubility	Aromatic hydrocarbons, chlorinated hydrocarbons
Iodine number	
Original GR-S	350
Soft cyclo GR-S	200
Hard cyclo GR-S	180–60
Compatibility	Parafin, GR-S
Moisture vapor transmission on glassine (compounded with 10% paraffin):	
Coating weight Lbs. per ream	M.V.T. Grams per sq. m. per 24 hrs.
0.7	4.08
2.4	1.79
3.5	1.09

and impart no taste or odor. The material shows promise also as an ingredient in moisture-, alkali-, and acid-resisting paints and lacquers, and as a reënforcing agent in GR-S wire coating compounds.

Other cyclized elastomers—The relatively dark color of cyclized GR-S and its insolubility in cheap petroleum hydrocarbons has encouraged work on other elastomers, such as polychloroprene, butadiene: acrylonitrile, butadiene: ethyl chloromaleate, isoprene: styrene, polyisoprene, and others.

The nitrile rubbers are very reluctant to undergo reaction, and require as much as 50 per cent of stannic chloride to produce a hard resin. No cyclization could be obtained with polychloroprene. The other rubbers behaved very much like GR-S, and by employing a suitable blend, it was found possible to obtain a cyclization product much lighter in color than cyclized GR-S and readily soluble in cheap petroleum hydrocarbons. This material compares favorably with the best-quality cyclized natural rubber in all properties excepting mechanical strength, which is not of importance in most applications. Its low solution-viscosity and rapid drying rate make it particularly well suited for applications involving the use of volatile solvents. In Table V a comparison is made with a low viscosity cyclized natural rubber.

TABLE V

COMPARISON OF A CYCLIZED SYNTHETIC RUBBER AND CYCLIZED NATURAL RUBBER IN SOLUTION VISCOSITY AND DRYING RATE

	Synthetic	Natural
Softening point	88° C	80° C
Viscosity of 20% solution (Secs. No. 4 Ford cup)		
Gasoline (low-boiling)	12	21
Toluene	13	23
V. M. & P. naphtha	15	52
Turpentine	30	179
Carbon tetrachloride	38	615
Drying time of 0.003 inch wet film (Seconds at 75° F and % relative humidity)		
Gasoline (low-boiling)	80	105
Toluene	140	145
Carbon tetrachloride	140	375
Turpentine	1350	2070
V. M. & P. naphtha	1620	2175

This cyclized synthetic rubber is finding application in many uses of importance to the war effort, and is rapidly replacing the cyclized natural product.

SUMMARY

By processes of cyclization and chlorination, synthetic elastomers can be converted into derivatives which differ from the parent product in the following respects:

1. Higher specific gravity.
2. Higher softening point.
3. Greater hardness and rigidity.
4. Less flexibility and elongation.
5. Greater chemical resistance.
6. Lower solution-viscosity.
7. Lower moisture-vapor transfer.
8. Lower moisture absorption.
9. Less tackiness.
10. Greater solubility in polar solvents.

Thus, many of the desirable features of the commercially important derivatives of natural rubber can be duplicated in synthetic products. It is, furthermore, logical to assume that the field of usefulness of synthetic derivatives will be extended by selection of the proper type of synthetic rubber for cyclization, chlorination, and hydrochlorination to bring out certain desirable characteristics which are not inherent in products made from natural rubber.

REFERENCES

[1] "Untersuchungen über die Natürlichen und Künstlichen Kautschukarten", Berlin, Julius Springer, **1919**.
[2] *J. Russ. Phys.-Chem. Soc.* **47**, 1915 (1915).
[3] *Kolloid Z.* **27**, 311 (1920).
[4] *Ind. Eng. Chem.* **19**, 1325 (1927).
[5] Bruson, U. S. patent 1,797,188 (1931).
[6] Endres, U. S. patent 2,052,391 (1936).
[7] Brit. patent 2,734 (1859).
[8] Peachy, U. S. patent 1,234,381 (1917).
[9] *Farben Ztg.* **37**, 552 (1932).
[10] *Ber.* **33**, 779 (1900).
[11] *Modern Packaging* **17**, No. 2, 103 (1943).
[12] Minich, *India Rubber World* **102**, No. 1, 51 (1940).
[13] Blomer, I. G. Farbenind, U. S. patent 2,222,345 (1940); U. S. patent 2,292,737 (1942); U. S. patent 2,301,926 (1942).
[14] Mol, *Ingenieur* **55**, 55 (1940).
[15] Koshelev *et al*, *Caoutchouc and Rubber* (*U.S.S.R.*), No. 8, 21 (1939); *India Rubber World* **108**, No. 1, 74 (1943).
[17] Frolich and Bannon, U. S. patent 2,327,517 (1943).
[18] Morrell, Frolich and Bannon, U. S. patent 2,334,277 (1934).

PROPERTIES OF HARD RUBBER. XI

EXPERIMENTS ON AGING

H. F. Church and H. A. Daynes

INTRODUCTION

In the course of the joint research with the British Electrical & Allied Industries Research Association on the properties of hard rubber in relation to composition and method of manufacture, it was necessary to study the absolute and relative aging characteristics of a number of rubber-sulfur compositions. There was little published information to guide the investigators. Compared with soft rubber, the durability of which depends on special care in manufacture, hard rubber is generally accepted as a relatively permanent material. Rapid deterioration due to oxidation, to which soft rubber is liable, is seldom encountered in hard rubber, and frequent replacement of hard rubber components is, therefore, unnecessary.

The only important published experimental work on the subject is that by Dieterich and Gray[1], who tested various hard rubbers of known history for cross-breaking strength, impact strength, and yield temperature before and after aging treatments in air ovens at 70° and 149° C. Their results were, briefly, as follows. Cross-breaking strength increased at 70° C, but was lowered by intermittent heating at 149° C for a total heating time of 60 hours. Impact strength (unnotched specimens) fell rapidly at both temperatures particularly at 149° C. Undervulcanized samples, although initially superior, lost strength more rapidly. Intermittent heating produced more rapid deterioration than continuous heating. Yield temperature was raised slightly by heating in air at 149° C for 15 hours, after which there was a decrease.

The present report describes experiments which were made to obtain information regarding the nature of the deterioration, the best properties to use as a measure of deterioration, and the aging periods required in aging tests. The experiments consisted of (1) cross-breaking strength, impact strength, and plastic yield tests on rubber-sulfur compositions of known history exposed to air at 70° C for various periods and in various forms, and (2) impact tests on some very old samples of ebonite of known origin.

METHODS OF TEST

CROSS-BREAKING STRENGTH AND ELONGATION

Cross-breaking strength and elongation were determined by the method of three-point loading, in which a bar of rectangular section is supported on two parallel rounded knife edges, and the load is applied centrally by another such knife edge. The method has already been described[2]. The quantities determined were the cross-breaking strength and elongation, these being the tensile strength and breaking elongation which would account for the actual

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breaking load and deflection at the center of the bar if the simple elastic laws held up to the breaking point.

The dimensions of test piece and other details were:

Length	7.5 cm.
Width	2.5 cm.
Depth (= thickness of sheet), about	0.5 cm.
Distance between outer knife edges	5.08 cm. (2 in.)
Radius of outer knife edges	$\frac{1}{16}$ in.
Radius of inner knife edge	$\frac{1}{8}$ in.
Rate of loading to break in about 1 minute as determined by preliminary tests.	

The most-stressed faces of the specimen were thus the original moulded faces of the sheet from which it was cut.

IMPACT STRENGTH

The impact strength of both notched and unnotched test-pieces was determined by the standard method of the Research Association of British Rubber Manufacturers, of which the following is a brief description:

A knife-edge is weighted and allowed to fall vertically between guides with a known velocity, *i.e.*, from a known height, on to the center of a straight strip of the material supported edgewise on two parallel and horizontal knife edges. The knife edge dimensions and spacing are the same as in the cross-breaking test. Two types of test piece are adopted, namely notched and unnotched. In the former, the notch is on the underside and midway between the supporting knife edges, so that the specimen is struck immediately over the notch. The following are the dimensions of the test pieces:

(1)	Unnotched	
	Length	7.5 cm.
	Depth	1.27 cm.
	Width about 0.5 cm. = thickness of sheet	
(2)	Notched	
	Length	7.5 cm.
	Depth (total)	1.9 cm.
	Width about 0.5 cm. = thickness of sheet	

A vertical notch, 6.3 mm. deep and rounded at the base to 1.6 mm. radius, is made across the center of the under surface of the test-piece by drilling a hole (52-gauge) through the test-piece perpendicular to the side face, and joining the hole to the nearest edge by a saw cut. The remaining depth of the test-piece is therefore 12.7 mm., equal to the total depth of the unnotched test-piece, so that the cross-sectional areas subjected to maximum stress are the same in both types of test-piece.

The most stressed faces of the impact specimen are thus not the moulded faces of the sheet but the surfaces which have been machined in preparing the specimen.

The energy required for fracture is expressed in kg.-cm. per sq. cm. of the nominal fractured section, and is determined as follows:

In the case of the unnotched test-piece, the knife loaded with a certain weight is released successively from heights of 10, 20, 30, 40 cm. and so on, until breakage occurs, the load being selected by preliminary tests so that, on the average, half the specimens are fractured by a blow from a height of 40 cm. The impact strength of each sample is regarded as the product of the falling weight per unit area of cross-section and the mean of the height which caused the break and the preceding height of release. The impact strength of the material is taken as the mean of the impact strengths, so defined, of the individual samples.

The same method is used for notched samples, except that the series of heights of fall is 5, 10, 15, 20, 25 cm. and so on, the load being selected so that, on the average, half the specimens are fractured by a blow from a height of 20 cm.

PLASTIC YIELD AND YIELD TEMPERATURE

The plastic properties were studied by a method already described[3], of which the following is a brief outline.

A rectangular strip is submitted to a torsional stress at a series of steady temperatures, preferably a new test-piece being used at each temperature, and the yield under this stress is measured at various times after application of the stress. On plotting yield after a given time against temperature of test, it is observed that at a fairly definite temperature, the yield begins to increase very rapidly with increase of temperature, the temperature-yield curve in the region of rapid yield being linear. The intercept of this linear portion, when produced to cut the temperature axis, defines the R.A.B.R.M. yield temperature, which, for hard rubber, is found to be independent of test-piece dimensions and the magnitude of the torque, but dependent on the period of application of the torque.

The following conditions of test have been adopted:

Length of test-piece between grips	7.5 cm.
Width of test-piece	1.5 cm.
Thickness of test-piece	0.5 cm.
Couple usually applied	75 g.-cm.
Duration of stress	30 min.

In cases where the deflection under standard torque would be greater than about 10 angular degrees, a lower torque is used and a correction is made accordingly, it having been found that the deflection after any given time is directly proportional to the torque at all temperatures of test.

DETERIORATION IN AIR AT 70° C (FIRST SERIES OF TESTS)

DETAILS OF TESTS

Several sheets (250 × 250 × 5 mm.) of rubber-sulfur (70:30) stock were vulcanized for 5 hours at 155° C by the usual method adopted in R.A.B.R.M. investigations, *i.e.*, the stock was first given a preliminary vulcanization in moulds slightly deeper than 5 mm. to allow most of the shrinkage to take place, the semivulcanized sheets then being transferred to moulds of the desired thickness in the autoclave press. In each case there was a uniform temperature rise of 55° C per hour to the vulcanizing temperature.

The properties tested before and after various periods of aging were (1) cross-breaking strength and elongation, (2) impact strength (notched and unnotched), and (3) plastic yield and yield temperature.

Since it was desirable to distinguish between the effects of surface oxidation and of charges in the bulk of the material, the samples for impact tests were aged both as sheet and as prepared test-pieces, the test-pieces in the former case being prepared immediately after removal of the sheets from the oven at the end of each aging period.

The aging was carried out in a ventilated air oven, automatically controlled at 70° C. The samples were supported in racks designed to give free access of air to all surfaces with a minimum of sagging due to softening at the high

temperature. Aging was continued in certain cases to 200 days but, as this long period was not anticipated at the beginning, the material was insufficient for all the tests to be so extended.

RESULTS

The results are shown in Tables I and II, the latter being data, obtained from smooth curves, from which the temperature-yield curves may be reconstructed.

TABLE I

CHANGING OF PROPERTIES DURING AGING IN AIR AT 70° C

Aging period (days)	Impact strength (kg. per cm. per sq. cm.*)				Cross-breaking properties (A)*		
	Unnotched		Notched				
	A	B	A	B	Strength (kg. per sq. cm.)	Elongation (percentage)	Yield temperature (°C)‡
0	65	65	4.4	4.4	1480	12.2	79.5
7	65	...	1.75†	3.5	1500	12.9	80
14	70	42	3.4	3.0	1500	12.1	80
28	76	27	2.4	2.35	1500	11.9	81.5
56	...	...	1.8	2.2	...	...	...
115	46	...	...	...	1490	11.5	...
200	55	...	...	...	1465	10.8	85

* A = test-piece cut from sheet after aging
* B = test-piece cut from sheet before aging
† A repetition with less samples gave 1.4
‡ To nearest 0.5° C

TABLE II

YIELD-TEMPERATURE PROPERTIES AFTER AGING IN AIR AT 70° C

Aging period (days)	Temperature (°C) required for a yield of			
	2.5	5.0	7.5	10.0 angular degrees
0	81.6	83.8	85.9	87.8
7	81.9	84.1	86.1	88.0
14	82.1	84.2	86.2	88.2
28	83.6	85.7	87.8	89.6
200	86.8	88.8	90.7	92.5

DISCUSSION OF RESULTS

As found by Dieterich and Gray[1], the properties measured by different tests are affected at different rates. Impact strength (unnotched, aged as test-pieces; notched, aged in both forms) falls to half value in about 20–40 days, but impact strength (unnotched, aged as sheet) at first rises and then begins to fall between 28 and 100 days, but probably nearer 100 days. Cross-breaking strength and elongation appear to be falling only slightly after 200 days.

Since some strength properties remain practically unimpaired, it appears that the bulk of the material must remain in good condition in spite of the aging. (For example cross-breaking strength has been maintained for ten times the period which would have sufficed for the perishing of most soft rubbers under the same conditions). This would occur if the deterioration were due to superficial oxidation.

One might expect, if this were the case, that tests in which the most-stressed faces (top and bottom during test) had been exposed during aging would develop weakness most rapidly. This is the case in the comparison between un-

notched samples aged in sheet and test-piece forms, but the similarity of behavior of the two forms of notched test-piece and the maintenance of cross-breaking strength then need further explanation.

The yield temperature is appreciably increased by the aging treatment, the temperature-yield curve being moved in the direction of higher temperatures without change of shape. This improvement in heat-resistant properties appears to be a direct result of the prolonged heating at a medium temperature, rather than to further vulcanization or oxidation, for (1) it is known from other experiments that this increase in yield temperature is not produced by four hours of extra vulcanization at 155° C (to which heating for 200 days at 70° C is estimated to be equivalent) and (2) it is improbable that a superficially oxidized layer could so control the sample under stress as to mask the normal softening of the unoxidized interior.

This change in yield temperature, which might be of considerable practical importance if it could be produced economically at will, may be due to something akin to polymerization, but it would be premature to speculate further without confirmatory experiments.

DETERIORATION IN AIR AT 70° C (SECOND SERIES, IMPACT TESTS ONLY)

DETAILS OF TESTS

To ascertain the role played by the various aged surfaces in reducing the impact strength of test-pieces, further experiments were carried out as follows. The material used was nominally the same as in the previous section, being prepared from the same rubber and sulfur in the same ratio, 70:30, and vulcanized for 5 hours at 155° C; but the preparation was carried out at a different date by a different investigator. The aging treatment was the same as before, namely storage in a ventilated air oven at 70° C, but the test-pieces were of different types as follows:

(1) Normal test-pieces, notched and unnotched, were cut from sheet after aging. The moulded side faces had thus been exposed to air, but the upper and lower faces and the inside of the notch, *i.e.*, the most-stressed faces, had not.

(2) Normal test-pieces, notched and unnotched, were cut from sheet before aging and were tested after aging without further treatment. All surfaces had thus been exposed to air during aging.

(3) Normal test-pieces, unnotched only, were cut before aging. After aging, a layer 0.75 mm. thick was removed from each moulded side face. The upper and lower faces only, *i.e.*, the most-stressed, had, therefore, been in contact with air during aging.

(4) Normal test-pieces, notched and unnotched, were cut from aged sheet and a layer 0.75 mm. thick was removed from each moulded side face. Thus, no face of the final test-piece had been exposed to air during aging.

(5) Test-pieces, unnotched only, having all the longitudinal edges rounded to 1 mm. radius but otherwise normal, were prepared before aging. After aging, they were tested without further treatment. Thus all surfaces had been exposed to air during aging, but there were no sharp edges at which oxidation might be particularly severe.

Twelve specimens of each type were tested initially and after each of the three aging periods. Types A and B correspond to those of the previous section, III, but C, D and E provide new information. The results are given in Tables III and IV.

TABLE III

EFFECT OF AGING IN AIR AT 70° C ON VARIOUS TYPES OF UNNOTCHED IMPACT STRENGTH TEST-PIECES

Aging period (days)	Impact strength (unnotched), kg. per cm. per sq. cm., of type				
	A	B	C	D	E
0	56	56	58	58	57
14	54	44	53	61	46
35	67	29	55	ca. 60	43
77	55	38	52	63	32

TABLE IV

EFFECT OF AGING IN AIR AT 70° C ON VARIOUS TYPES OF NOTCHED IMPACT STRENGTH TEST-PIECES

Aging period (days)	Impact strength (notched) (kg. per cm. per sq. cm., of type)		
	A	B	D
0	6.1	6.1	6.1
7	5.3	3.7	...
19	4.4	2.8	6.8
63	7.0	2.7	5.8

RESULTS

These results are plotted in Figures 1 and 2, those from Table I being added in broken line for comparison. The following discussion will relate to both sets of results.

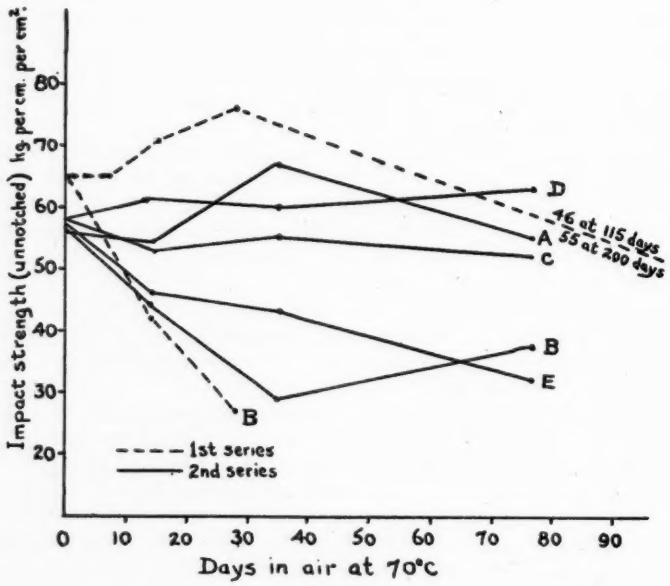


FIG. 1.

DISCUSSION OF RESULTS

It has been found in impact testing, whether on aged or new material, that abnormal mean results for a group of similar samples occur fairly frequently.

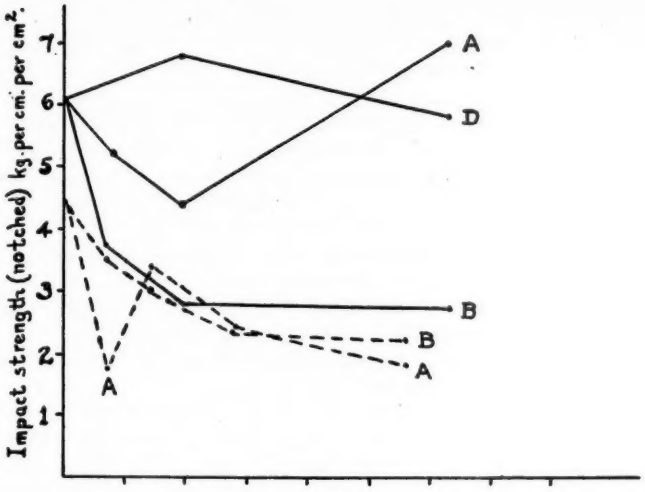


FIG. 2.

These usually appear to be due, not to variations in testing technique, but to real variations in the material; for if fresh groups of samples of the same material are prepared and tested, the abnormal results are usually confirmed. It appears that impact strength, and possibly also its fall during aging, is very sensitive to untraced variables in the material. In the present set of results there are irregularities of this kind which make some of the results appear contradictory and so difficult to interpret. However, there are still some definite conclusions to be drawn.

1. *Type A.*—When the exposed surface is entirely removed before testing, the remaining material (notched and unnotched) is found to be unimpaired during the aging periods of 63–77 days.

2. *Type B.*—When all the exposed faces are retained during test, the impact strength (notched and unnotched) falls considerably within periods as short as 7 days. Observations 1 and 2 are in accord with the view that the loss of strength is due entirely to superficial oxidation.

3. *Type C.*—When the only exposed surfaces retained during test are the most-stressed (top and bottom) faces, the impact strength is practically unaffected by aging. (Unnotched samples only were tested in this case).

4. *Type A.*—With unnotched samples, when the only exposed surfaces retained for test are the side-faces, there is practically no loss of strength on aging for 77 days. There is some loss at 100–200 days, but there are no results for this period on other types of test-piece for comparison.

The results from notched test-pieces are less consistent, but there is a definite fall of strength in one case, while the values are irregular in the other, the result of 63 days' aging being an appreciable improvement after what appeared to be a steady fall up to 19 days.

5. *Type E.*—Observations 2, 3, and 4 on unnotched test-pieces indicate that a combination of exposed faces on all sides of the aged specimen may be necessary for it to show a marked loss of strength, as if the aging along sharp edges had some special effect. The test on the samples aged with rounded edges does not support this explanation; for the fall in strength in this case is not

very different from that of type (B), which differs from type (E) only in having sharp edges.

It is quite clear that the aging of hard rubber cannot be considered precisely except in relation to the form of the material and the type of stress to which it is subjected. The strength falls off rapidly in an impact test (unless exposed surfaces are removed), whereas it is maintained in a cross-breaking test where the stress is applied slowly; and there may be differences in certain cases (Type A) between the rates of loss of strength of notched and unnotched samples. The results of tests in which only some of the faces of the test-piece have been exposed during aging are not consistent with a simple theory that fracture is determined by weakness at the most-stressed face.

Although there are many doubtful points which still require investigation, it can be concluded that, for a quick test of stability of a hard rubber material, notched and unnotched impact test-samples may be aged in test-piece form. However, in interpreting the results, it must be remembered that the material made up in other shapes than those tested and subjected to other types of stress, *e.g.*, cross-breaking, would not break down in practical use in a comparable time, even if exposed to the same atmospheric conditions. Also, such tests must at present be used only as a measure of stability under the conditions of test. There is no evidence in the tests just described that a material which breaks down after aging at 70° C is likely to become defective in any way on continued use at ordinary temperatures.

Further study of the influence of form of the sample on its rate of loss of strength on aging is of considerable practicable importance, for, as a result, it might be possible to recommend methods of construction in which the strength of the component would be maintained in spite of oxidation of the exposed surface of the insulating material.

NATURAL AGING OF HARD RUBBER OVER LONG PERIODS

DETAILS OF TESTS

Although hard rubber is usually accepted as a stable material, not subject to oxidation during storage as soft rubber is, it was decided to collect and make some confirmatory tests on samples of hard rubber which were known to be of great age. It was difficult to obtain much material of suitable age and known history, but two hard-rubber manufacturing members of the Research Association of British Rubber Manufacturers supplied four samples, the available particulars of which are given below. Exact measurements of the loss of strength are impossible, since measurements on the original materials are not available, but it is possible to judge in most cases whether there has been any serious deterioration. In two cases the composition is indefinite, and in a third the nature of the accelerator is not stated, although, in view of the date of manufacture, it is probably an inorganic material which would reduce the strength slightly.

Samples (1) and (2) appear to have been stored in the dark or in diffused light, for the surfaces of the sheet are black and polished. Sample (3) was apparently loaded to some extent, and the raspings were darker in color than is usual with a pure rubber-sulfur mixing. Sample (4) was an instrument panel which had evidently been for many years in sunlight, for the surface was a bright yellow, and showed a fine network of slight cracks when treated with boiling water, dried and viewed under the microscope. The density was that of a pure rubber-sulfur composition.

Where possible, samples were cut, first, entirely from the interior of the material, and, secondly, including the original outer surface as the top and bottom of the test-piece. The quantity of material was very limited, so only unnotched pieces were tested. In the only case possible, the value for unaged material expected from the results of the R.A.B.R.M. tests is included in Table V.

RESULTS

TABLE V

IMPACT STRENGTH OF OLD SAMPLES OF HARD RUBBER

Sample	Age (years)	Composition	Impact strength (kg. per cm. per sq. cm.) 1	2	3
(1)	19	Rubber 65.0, sulfur 32.4, accelerator, 2.6	33	32	...
(2)	24	Rubber 66.67, sulfur 33.33	49	47	55
(3)	approx. 30	Hexagonal nut; unknown composition; density 1.257	6.8	...	...
(4)	20–25	Instrument panel, with discolored surface; density 1.20	34	5.9	...

Notes: 1. Cut from interior
2. Aged faces on top and bottom of test-piece
3. R.A.B.R.M. test on similar rubber-sulfur composition

DISCUSSION OF RESULTS

In samples (1) and (2), which have apparently been stored away from bright light, the impact strength is still good, whether the test-piece is cut from the interior or not, and is probably little if any lower than initially.

The strength of sample (3) is low, but whether it was originally stronger is doubtful in view of its uncertain composition. In view of the loading materials present and the possibility that dust was used to obtain fine moulding screw thread, an initial strength as high as 55 is very improbable.

Sample (4), in spite of the severe exposure to light, has a high impact strength in the interior, but the damaged surface causes a serious fall in strength when included in the test-piece. Comparison may be made with the tests of type (C) test-piece in Table III, in which aged top and bottom surfaces did not reduce the strength. It is probable that, in the very old material (4), the damage extends more deeply into the material.

Generally it may be concluded, from the tests on old samples, that hard rubber can still be regarded as practically perament under ordinary storage conditions, but that reduction of impact strength may occur on prolonged exposure or in bright light.

SUMMARY

Tests have been carried out to find how the mechanical properties of hard rubber change with age.

On prolonged exposure of the whole specimen to air at 70° C, the impact strength of notched and unnotched test-pieces may fall by 50 per cent or more. On the other hand, the plastic yield temperature increases appreciably with 200 days' exposure. The conditions affecting the improvement in such an important property are worthy of further serious study.

When certain faces of the specimen are protected from the air, the rapid loss of impact strength does not take place, and cross-breaking strength may remain unimpaired for as long as 200 days. The deterioration on aging appears to be confined within a very short distance of the surface, the bulk of the material retaining its full strength for very long periods. The retention of strength when certain faces are protected may have an important bearing on questions of design.

Examination of old samples of hard rubber shows that the mechanical properties remain good under ordinary conditions of storage for periods of 20–30 years, but that weakness may be caused at surfaces which are severely exposed to sunlight.

REFERENCES

[1] Dieterich and Gray, *Ind. Eng. Chem.* **18**, 428 (1926).
[2] Church and Daynes, *Trans. Inst. Rubber Ind.* **13**, 96 (1937); RUBBER CHEM. TECH. **11**, 224 (1938).
[3] Church and Daynes, *J. Rubber Research* **8**, 41 (1939); RUBBER CHEM. TECH. **12**, 826 (1939).

PROPERTIES OF HARD RUBBER. XIII

EXPERIMENTS ON THERMAL EFFECTS DURING VULCANIZATION *

H. F. Church and H. A. Daynes

INTRODUCTION

Preceding reports in this series have contained accounts of results obtained during the investigation which has been conducted by this Research Association, in coöperation with the British Electrical & Allied Industries Research Association, on the properties and methods of testing of hard rubber.

In planning this investigation, it was foreseen that care would have to be taken to control the thermal conditions in the interior of the hard rubber specimens during the vulcanization process. This report describes some preliminary tests made to obtain information as to the factors affecting those conditions.

It is well known to rubber technologists that the heat produced by this reaction will, under certain conditions, cause an appreciable internal rise of temperature, which may, according to its intensity, increase the rate of vulcanization above that intended, produce porosity, or, in extreme cases, cause violent explosions. This tendency towards internal heating is enhanced (1) by raising the vulcanization temperature; (2) increasing the thickness of the material; (3) increasing the speed of the reaction by the use of accelerators, or (4) decreasing, if possible, the content of nonreactive components, such as hard rubber dust or mineral ingredients. Internal heating is one of the serious limiting factors in hard rubber production, and the facts outlined above are common knowledge. The phenomenon is also of great theoretical interest, and several investigators have studied the variations of the internal temperature with period of time during vulcanization[1].

For the purpose of the joint research with the Electrical Research Association, it was required to vulcanize a number of sheets of different hard rubber mixings at various temperatures and to study the properties of the materials produced. In the preparation of the specimens it was obviously described to obtain material free from porosity, and it was necessary also for the two following reasons to avoid any internal temperature rise of even a few degrees.

(1) If any such rise occurred, the actual temperature within the specimen would be at variance with the observed externally applied temperature, and any conclusions based on the latter would thus be vitiated. The necessity of knowing accurately the real vulcanizing temperature will be realized when it is remembered that the rate of vulcanization increases by about 10 per cent per 1° C, and that at one stage of vulcanization an increase of that amount would make a difference of 8° C in the plastic yield temperature.

Moreover, any variables, such as composition or applied temperature of vulcanization, the effects of which it was required to study, would themselves alter the excess temperature of the material above that of the applied temperature of vulcanization, and so complicate the issue by varying the real vulcanizing temperature.

* Reprinted from the *Journal of Rubber Research* of the Research Association of British Rubber Manufacturers, Vol. 13, No. 5, pages 55–58, May 1944.

(2) Internal rise of temperature would cause variation in properties at different depths in the sheet, the center being more fully vulcanized than the outer layers. The effective mean state of vulcanization would then be indefinite and would vary according to the property being tested, and in many cases according to the direction in which the test piece was cut.

As the literature does not contain any information directly applicable to the problem of estimating the rise of temperature in sheets vulcanized between platens, a few experiments were carried out to determine the influence of thickness and vulcanizing temperature in the type of mixing in question, namely, an unaccelerated rubber-sulfur mixing.

It would have been preferable to carry out the experiments in the light of a complete mathematical theory of the temperature changes in terms of thermochemical data for the reaction and the physical constants of the material. Some progress has been made with such a theory, but not to a stage where a useful report can be made on this aspect of the question. Not only is the mathematical problem very complicated, but accurate data as to the dynamics of the reaction are lacking. However, the elements of the problem may be seen from the following considerations.

The heat of vulcanization of a rubber-sulfur (68:32) mixing to the state of hard rubber is about 300 calories per gram of vulcanizate[2], and the specific heat of the vulcanizate is about 0.33 calories per gram per 1° C. If all this heat could be retained without decomposing the material, it would be sufficient to raise its temperature to about 1000° C, so the dissipation of most of the heat by conduction is essential to the production of a satisfactory vulcanizate from such a mixing.

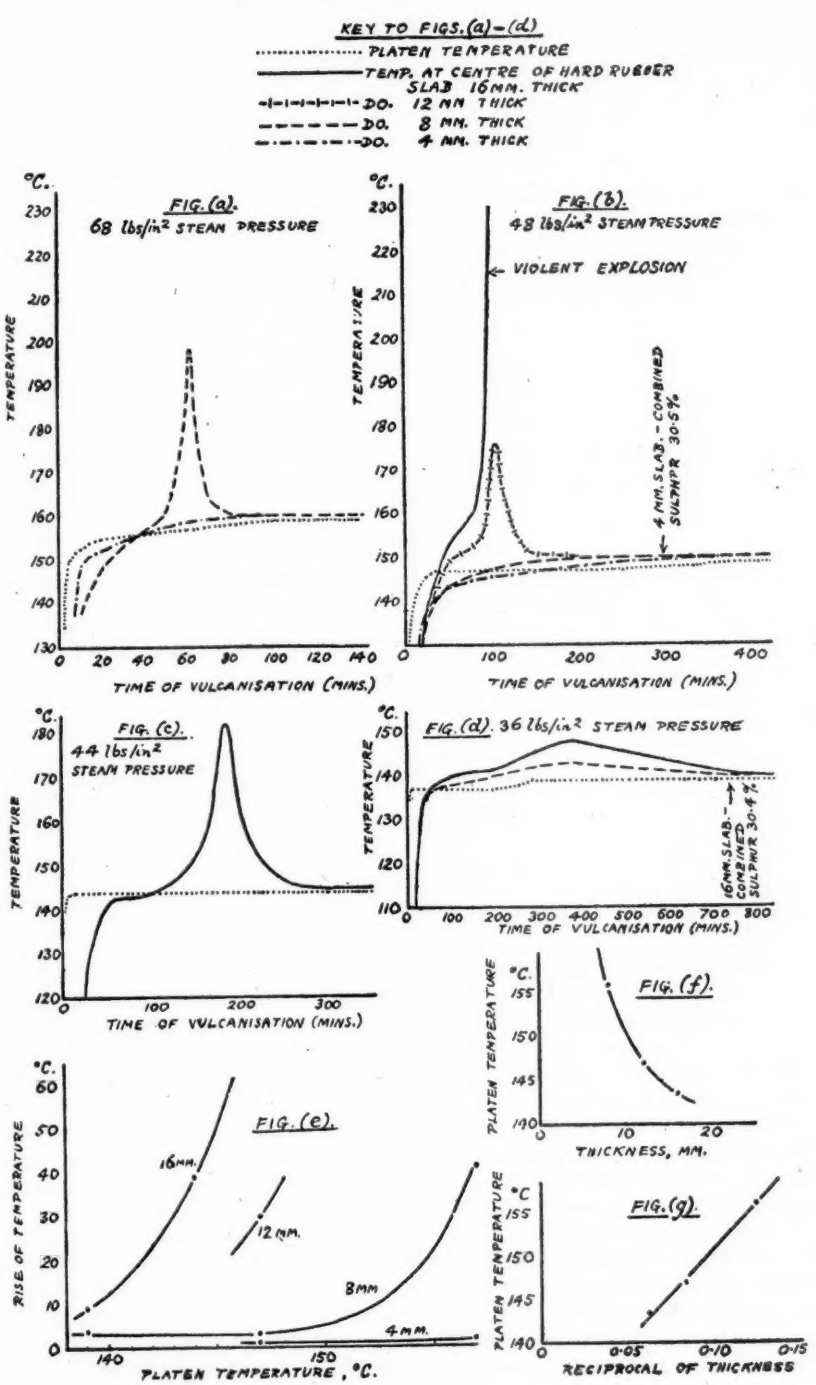
The rate of production of heat per cc. at any point in the material depends on the local temperature, on the proportions of the reacting materials, rubber, sulfur, and accelerator if any, and on the concentration of nonreacting materials. The rate of dissipation of heat depends on the difference between the local and the surface temperatures, the distance of the point under consideration from the surface, and the thermal conductivity of the material.

If the rate of production of heat is sufficiently low, an internal rise of temperature of, say, a fraction of one degree, may be sufficient to cause conduction of the heat produced to the surface, and the temperature thus remains substantially uniform and equal to the applied vulcanizing temperature. On the other hand, with a high rate of production of heat, a considerable internal rise of temperature may occur before a temperature gradient sufficient to conduct the heat away is established. This increases the reaction rate still further and causes a more rapid rise of temperature so that the system may be unstable, the temperature continuing to rise at an increasing rate till decomposition results. Between these two extremes there are cases in which a large but limited rise of temperature occurs, the rise being arrested by the increased rate of conduction by the absorption of heat in raising the temperature of the material, and by the exhaustion of the reactions, *i.e.*, by the saturation of the rubber or combination of all the sulfur. All these cases will be illustrated by the experimental work to be described below.

EXPERIMENTAL

DETAILS OF EXPERIMENTS

Sheets of rubber-sulfur (65:35) stock of thicknesses 4, 8, 12, and 16 mm. were vulcanized in rectangular spacing moulds at various steam pressures


KEY TO FIGS.(a)-(d)
PLATEN TEMPERATURE
TEMP. AT CENTRE OF HARD RUBBER SLAB 16MM. THICK
DO. 12 MM THICK
DO. 8 MM. THICK
DO. 4 MM. THICK
FIG.(a).
68 lbs/in² STEAM PRESSURE
TEMPERATURE °C.
TIME OF VULCANISATION (MINS.)
FIG.(b).
48 lbs/in² STEAM PRESSURE
VIOLENT EXPLOSION
4 MM. SLAB. - COMBINED SULPHUR 30.5%
TEMPERATURE °C.
TIME OF VULCANISATION (MINS.)
FIG.(c).
44 lbs/in² STEAM PRESSURE
TEMPERATURE °C.
TIME OF VULCANISATION (MINS.)
FIG.(d). 36 lbs/in² STEAM PRESSURE
16MM. SLAB. - COMBINED SULPHUR 30.4%
TEMPERATURE °C.
TIME OF VULCANISATION (MINS.)
FIG.(e).
16MM.
12 MM.
8MM
4MM.
RISE OF TEMPERATURE °C.
PLATEN TEMPERATURE, °C.
FIG.(f).
PLATEN TEMPERATURE °C.
THICKNESS, MM.
FIG.(g).
PLATEN TEMPERATURE °C
RECIPROCAL OF THICKNESS

from about 35 to 70 lbs. per sq. in. A fine wire thermocouple was embedded in the center of each sheet, and the temperature was read on a direct-deflection galvanometer. The platen temperature of the press was assumed to be the same as the steam temperature, which was determined by thermocouples within the platens. All the thermocouples were compared directly in an oil-bath before the tests. Since the heating to be expected was considerable, no special precautions were taken to secure great accuracy in temperature control or measurement, so the excess internal temperature is uncertain in some cases to the extent of a degree or two. The moulds containing the stock were placed cold in the daylight press, and time was measured from the instant of turning on steam. Temperature readings were then taken at intervals of 10 minutes, or less when necessary, over a sufficient period to complete vulcanization at the platen temperature. The time-temperature curves so obtained are shown in Figures (*a*)–(*d*). They are of the type found by previous workers, *i.e.*, the internal temperature first lags behind the platen temperature but soon rises above it to a maximum, corresponding approximately to the state of vulcanization at which the rate of heat production is a maximum, and then falls to approach the platen temperature asymptotically as the reaction nears completion.

RESULTS

The rise of temperature at the maximum is shown in Table I and is plotted against platen temperature in Figure (*e*), each curve corresponding to one

TABLE I

RISE OF INTERNAL TEMPERATURE UNDER VARIOUS CONDITIONS (PRESS)

Platen temperature (and equivalent steam pressure lbs. per sq. in.)	Rise of temperature (°C) in sheets of thickness (mm.)			
	4	8	12	16
157° C (68)	2	41	...	...
147° C (48)	1	3	30	80 (explosion)
144° C (44)	...	...	...	39
139° C (36)	...	4	...	9

thickness of sheet. The platen temperature which causes an excess temperature of 30° C in the interior of the hard rubber has been estimated, and is plotted against thickness and reciprocal of thickness in Figures (*f*) and (*g*) respectively, the values being read from the smooth curves in Figure (*e*); owing to the few points in the latter curves, however, the results are not very accurate.

Some sheets of hard rubber 16 mm. and 8 mm. thick and of a different rubber-sulfur (68:32) mixing were vulcanized at about 48 lbs. per sq. in. steam pressure, and the time-temperature curves were found to be almost indistinguishable from the corresponding curves for the 65:35 mixing.

It has been found also that the rise in internal temperature is greater when the material is vulcanized suspended in open steam than when vulcanized in a press. This result is as anticipated, since the steam is not able to conduct heat away from the surface of the sheet so readily as the metal platens, so that the outer faces of the sheets rise above the temperature of the steam. The results obtained with two thicknesses of sheet are shown in Table II.

TABLE II

RISE OF INTERNAL TEMPERATURE (OPEN STEAM)

Platen temperature	Thickness of sheet (mm.)	Rise in temperature
152° C	4	5° C
152° C	8	42° C

DISCUSSION OF RESULTS

(1) The curves connecting time and internal temperature are of a familiar type, the effect of the rise of temperature due to the reaction varying from a slight convexity to a sharp peak rising about 40° C above the platen temperature, or a continuous rise ending in an explosion.

(2) The internal rise of temperature depends greatly on the vulcanizing temperature, the choice of a safe temperature being very critical. The internal heating may vary from a negligible amount to an excessive rise of 40° C within a range of 10° C in the vulcanizing temperature.

(3) With each vulcanization temperature, the choice of a safe thickness of sheet is very critical. At 147° C, for example, a sheet 16 mm. thick explodes, while a sheet of half the thickness remains practically at platen temperature throughout the vulcanization period. It is seen from Figure (*g*) that, over a short range, the relation between the reciprocal of thickness and the vulcanization temperature causing a given rise of internal temperature is approximately linear. To obtain reasonably homogeneous sheets with vulcanizing temperatures up to about 160° C (75 lbs. per sq. in. steam pressure) it is necessary to use sheets not more than 5 mm. thick (see Figure (*e*)). The methods of test used in the joint research on hard rubber have, therefore, been selected so as to use test pieces cut from sheets of this thickness.

(4) The conditions of vulcanization in open steam are such as to enhance the heating effect compared with press vulcanization between platens.

(5) The relations among thickness, platen temperature, and temperature rise found in this work are of obvious interest to makers of hard rubber articles, although it must be pointed out that the numerical results obtained are not directly applicable to mixings of a different type or to objects of a different shape from sheets. It is not possible at this stage, for example, to indicate the thermal effects of such devices as the use of loading ingredients and hard rubber dust, or the method of building up thick objects in semivulcanized plies. In that connection a mathematical theory of the temperature rise in terms of the chemical and physical constants and dimensions of the material would be most valuable.

(6) These results are of interest to users of insulating materials also. The results of the joint research on hard rubber give information concerning the mechanical and electrical properties which may be expected from various rubber-sulfur compositions vulcanized for various periods and at various temperatures. It will be appreciated, however, in the light of this report, that it is not always practicable to produce commercial material from such simple mixings in all sizes and shapes and at a low cost. To secure at a reasonable cost the best properties of which hard rubber is capable calls for much skill in design as well as in manufacture. For example, in moulded components, much could no doubt be done to facilitate manufacture from the best materials by the avoidance of thick portions and by the judicious use of metal inserts which would serve to conduct heat away from the interior during vulcanization.

SUMMARY

The characteristics and technical importance of the internal heating effect during the vulcanization of hard rubber, due to the exothermic reaction between rubber and sulfur, are recalled, and the conditions under which thermal instability may occur are outlined. The necessity of avoiding even slight increases in internal temperature when vulcanizing material for research purposes is emphasized.

Experiments are described in which sheets of rubber-sulfur mixings of various thicknesses were vulcanized in a platen press at various temperatures, and the internal and surface temperatures were measured throughout the vulcanization period by means of thermocouples. The time-temperature curves are reproduced.

The relations between internal temperature rise, platen temperature, and thickness of sheet are indicated. The choice of maximum safe thickness for a given platen temperature or of maximum safe platen temperature for a given thickness is shown to be very critical.

The rise of temperature is greater in open steam vulcanization than in press-vulcanization, for a reason which is pointed out.

It is important that these limiting factors in the use of high-grade rubber-sulfur materials should be taken into account in designing hard rubber articles.

REFERENCES

[1] Williams and Beaver, *Ind. Eng. Chem.* **15**, 255 (1923); Toyabe, *J. Soc. Chem. Ind. Japan* **33**, 96B (1930); RUBBER CHEM. TECH. **3**, 384 (1930); *J. Soc. Chem. Ind. Japan* **33**, 275B (1930); RUBBER CHEM. TECH. **4**, 190 (1931); *J. Rubber Soc. Japan* **2**, 251 (1930); RUBBER CHEM. TECH. **4**, 514 (1931); Riding, *Trans. Inst. Rubber Ind.* **6**, 230 (1930); Blake, *Ind. Eng. Chem.* **22**, 737 (1930); RUBBER CHEM. TECH. **3**, 631 (1930); Hada, Fukaya and Nakajima, *J. Rubber Soc. Japan* **2**, 389 (1931); RUBBER CHEM. TECH. **4**, 507 (1931); Hada and Nakajima, *J. Soc. Rubber Ind. Japan* **5**, 288 (1932); RUBBER CHEM. TECH. **6**, 56 (1933).

[2] Blake, *Ind. Eng. Chem.* **22**, 737 (1930); RUBBER CHEM. TECH. **3**, 631 (1930).

CHANGES IN PHYSICAL PROPERTIES OF HARD RUBBER SHORTLY AFTER VULCANIZATION *

H. A. DAYNES

Preparatory to a full investigation of the properties of various specimens of hard rubber, it was considered necessary to decide on a minimum time interval between vulcanization and testing. This was desirable to allow specimens to attain a stable condition, and thus to avoid anomalies which might result from testing during a transition period, soon after vulcanization, when the physical properties are changing relatively rapidly. It was necessary to approach the problem from the standpoint of the following properties which it was desired to investigate.

CROSS-BREAKING STRENGTH AND ELONGATION

The first tests were carried out on cross-breaking properties, since the test-pieces are easy to prepare and tests can be carried out within an hour or so of vulcanization.

The material was an unloaded hard rubber prepared from 65 parts of smoked sheet and 35 parts of sulfur, and vulcanized in two stages for a total of 5 hours in a daylight press at 153° C, after a rise of 1 hour before each stage. The sheets were $\frac{3}{16}$ inch thick.

Test pieces $3 \times \frac{1}{4} \times \frac{3}{16}$ inch were cut and tested, as usual (see *J. Rubber Res.* **7**, 123 (1938)) for cross-breaking strength and elongation with a 2-inch distance between the outer knife-edges. These tests were carried out at intervals of 1.5 hours, 24 hours, 13 days, and 35 days after vulcanization. The rate of stressing was such as to break the samples in about 5 minutes. The results are shown in Table I.

TABLE I

Interval of time after vulcanization	Cross-breaking strength (lbs. per sq. in.)	Mean	Apparent breaking elongation (percentage)	Mean
1.5 hours	16,500		14.9	
	16,600	16,550	16.6	15.8
24 hours	15,900		13.9	
	16,500	16,230	15.2	14.4
	16,300		14.2	
13 days	17,750		13.8	
	17,650	17,660	12.3	13.5
	17,600		14.3	
35 days	17,300		12.1	
	17,200	17,130	14.1	12.9
	16,900		12.4	

* Reprinted from the *Journal of Rubber Research* of the Research Association of British Rubber Manufacturers, Vol. 12, No. 12, pages 131–132, December 1943.

The changes observed are not very great, but there appears to be a definite tendency for the early strength results to be a few per cent low and the early elongation results high. As far as these results go, an interval of not less than two weeks between vulcanization and testing seems desirable, although further experiments may show that a reduction in this time is justifiable.

TENSILE STRENGTH, ELONGATION, AND YOUNG'S MODULUS

Since the time factor appeared to be appreciable in cross-breaking properties, arrangements were made for some tensile and plastic yield tests on similar lines.

The material in these cases was an unloaded one consisting of 68 parts of smoked sheet and 32 parts of sulfur. Vulcanization was carried out at 149° C in a daylight press and for two different periods in order to contrast the properties of an under-vulcanized and a fully-vulcanized material. The vulcanization periods were respectively: 4 hours in two stages after rises 1 hour and 0.5 hour; and 9.5 hours in three stages after rises of 1 hour, 0.5 hour, and 0.5 hour.

TABLE II

Vulcanization (hours at 149° C)	Interval after vulcanization (days)	Tensile strength (lbs. per sq. in.)	Mean	Breaking elongation (percentage)	Mean	Young's modulus (lbs. per sq. in.) $M \times 10^3$	Mean
4	1	8300	8510	4.22	4.53	394	394
		8720		4.83		394	
	9	8780		3.83		403	
		9060	8910	4.30	4.20	388	396
		8900		4.48		397	
	34	9060		4.60		406	
		9007	9065	4.50	4.55	404	395
		(5970)		(1.64)		376	
9½	1⅞	9500	9660	4.27	5.00	401	398*
		9820		5.73		394	
	9	9730		5.56		352	
		9770	9727	5.72	5.44	382	372*
		9680		5.03		382	
	33	9530		5.48		385	
		9700	9620	5.63	5.56	391	381*
		(7300)		(2.25)		366	

Notes: (1) Figures in parentheses are not included in the mean values.
(2) The sheets from which those samples marked * were cut were appreciably curved, making the zero reading on the extensometer uncertain and the elasticity figures unreliable. However, the effect of this zero error on the elongation at break is small.

The results given in Table II show tensile strength breaking elongation, and an approximation to Young's modulus of elasticity, calculated from the elongation at a stress of 5000 lbs. per sq. in. The test method adopted was the usual method of this laboratory and the rate of stressing was 1600 lbs. per sq. in. per min.

The only property which appears to change appreciably with time is the tensile strength, and this only with the under-vulcanized material. In all other cases the variations with time are no more than the differences between individual results on duplicate samples. The change observed in tensile strength appears practically to have ceased after 9 days.

PLASTIC FLOW

The materials tested as above for tensile properties were also tested for plastic flow 1 week and 6–7 weeks after vulcanization. The following properties were investigated: (1) Yield temperature as defined by the R.A.B.R.M. (see *J. Rubber Res.* **8**, 41 (1939)); (2) Yield after 30 minutes under constant torsional stress at 65° C (4-hour sample) and 90° C (9.5-hour sample), these temperatures occurring about the center of the linear portions of the temperature-yield curves, and (3) temperature for yield of a fixed amount in 30 minutes.

The influence of time appeared in both cases to be in the direction of making the material more heat-resistant, but since the property is very sensitive to vulcanization (especially when the material is undervulcanized), and since it is difficult to ensure exact uniformity of vulcanization of a large sheet in the daylight press, it is recommended that this effect should be confirmed by new tests on material vulcanized in the autoclave press.

PROCESSING CHARACTERISTICS OF SYNTHETIC RUBBERS AND THEIR USE IN THE MANUFACTURE OF EXTRUDED PRODUCTS*

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The difference in processing behavior between synthetic rubbers and natural rubber becomes evident when production facilities designed for processing natural rubber are used for synthetic rubbers. All the synthetic rubbers in one respect or another are harder to process than natural rubber. Under circumstances other than the present emergency, processing equipment suitable for handling the synthetic rubbers would gradually be evolved. In the present situation, synthetic rubbers must be processed with equipment already available. In this discussion natural rubber and the general purpose synthetic rubbers, GR-S, GR-M and GR-I, will be considered.

The processing of dry rubber consists essentially of the incorporation of vulcanizing agents, pigments, oils, and other ingredients by a process of kneading, followed by the forming of the mix by extrusion or calendering into shapes suitable for fabrication preparatory to final cure. The mixing step, which is accomplished on a two-roll mill or in an internal mixer, requires that the rubber be within a plasticity range that will permit satisfactory dispersion of the ingredients. If the plasticity is too low the rubber tends to crumble, and if it is too high dispersion is poor. Crude natural rubber is quite tough, and before breakdown has some of the properties of vulcanized rubber, such as high recovery after moderate distortion. In the crude state it is extremely difficult to obtain satisfactory dispersion of pigments. It is therefore necessary to soften it by mastication or other means so that the pigments are more readily incorporated and power requirements are lowered. In addition, its nerve or tendency to recover after distortion is greatly reduced. Synthetic rubbers, in general, differ from natural rubber in their susceptibility to softening by mastication, and they show different relationships between nerve and plasticity than does natural rubber.

An instrument that has been found useful in studying the processing characteristics of the synthetic rubbers is the Mooney viscometer[1]. This instrument indicates the torque required to turn a rotor at constant speed in a confined sample of elastomer maintained at a constant temperature. Changes in viscosity with time in the viscometer, either toughening or softening, result from a shearing action which parallels under somewhat different conditions the changes which take place on a mill or in an internal mixer.

Figure 1 illustrates typical viscosity-time curves obtained by using the Mooney viscometer with samples of the crude, unmasticated elastomers under consideration. Several of them show an increase in viscosity following the

* This is one of thirteen papers comprising a "Symposium on the applications of synthetic rubbers" at the 1944 Spring Meeting of the American Society for Testing Materials, held at Cincinnati, Ohio, March 2, 1944. It is reprinted here from the Society's booklet containing the complete symposium.

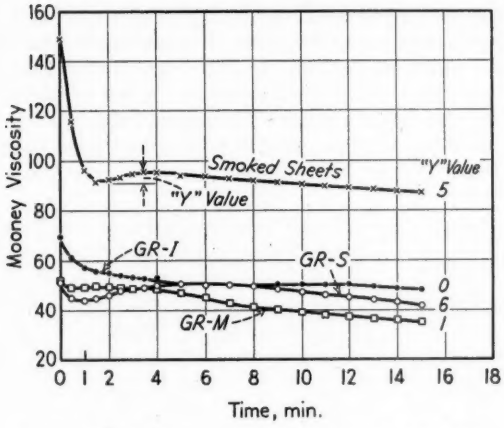

FIG. 1.—Viscosity-time curves. All tests made at 212° F.

initial minimum. This increase, indicated by the "Y" value on the curve, is thought to be a fundamental property of the rubber, determined by its composition and the conditions during polymerization, coagulation and drying. Since the rubber during this test is subjected to a shearing action analogous to that obtained in milling, it would be expected that milling prior to testing would change the shape of the curves. This is found to be the case, at least for all those rubbers which show a change in viscosity with time in the viscometer. A high "Y" value indicates that the rubber becomes tougher after moderate milling and that greater power is required for mastication. A reduction in viscosity after the peak has been reached indicates that softening takes place on mastication. In the case of GR-I there is no such reduction, which checks with the experience that mastication of the crude rubber is almost completely ineffective in changing the plasticity.

GR-S may be plasticized by hot or cold mastication on mills, by hot air treatment, or by passing through a Gordon plasticator. Figure 2 shows the

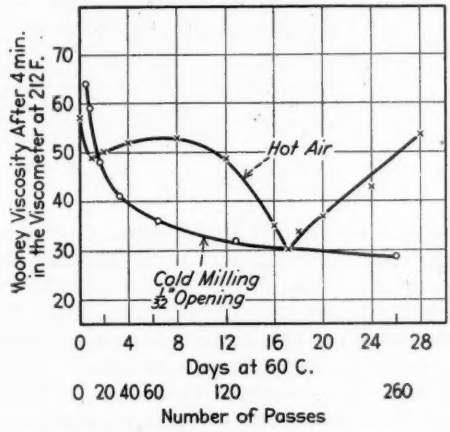

FIG. 2.—Comparison of effects of hot-air softening and cold mastication of GR-S.

effect for a typical sample of GR-S of heating in air at 60° C and of cold milling on the Mooney viscosity results after 4 minutes in the instrument. The changes that take place on heating are attributed to two competing reactions. During the early portion of the treatment, oxidative breaking of the molecules predominates; in the latter portion "oxygen vulcanization" predominates. Some degradation in physical properties determined after vulcanization accompanies the first type of reaction, and considerably more takes place during the

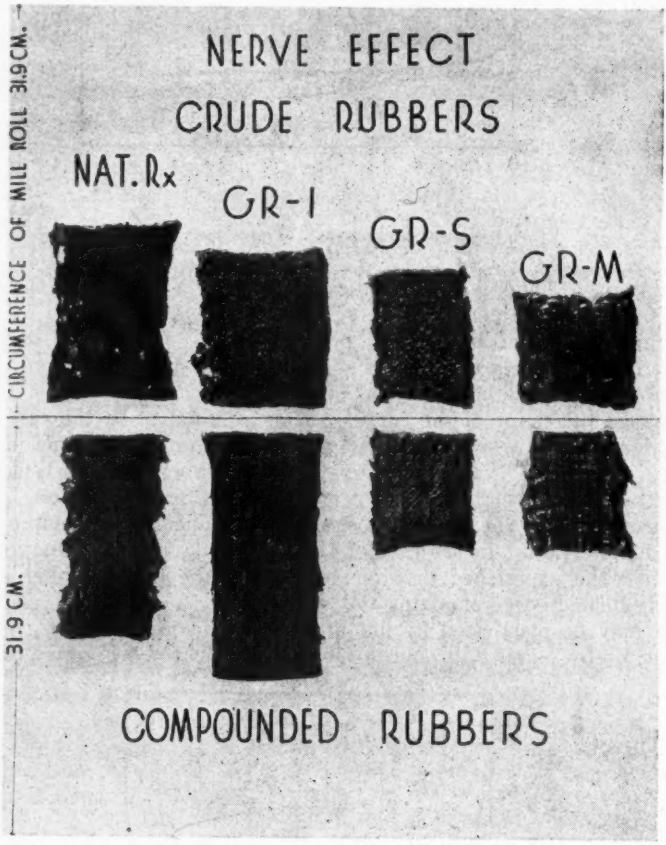

FIG. 3.—Nerve effect.

second. Cold milling may not involve any "oxygen vulcanization". At least there was no evidence of increased viscosity up to 264 passes through the mill.

One of the processing properties of considerable importance is the degree of nerve present in the rubber before and after pigmentation. Nerve as indicated above is shown by the tendency of a distorted sample of rubber to return to its original shape when the distorting force is removed. A test we have used to measure this property is to masticate a fixed volume of rubber on a laboratory mill for a definite time at a constant roll temperature and mill opening. The rolls are then opened so that the bank just disappears, and the rubber is

cut off and allowed to shrink freely. The difference between the final length of the sample and the circumference of the roll is a measure of the nerve present. The shrinkage obtained in this test can be varied greatly by altering the time, temperature, and mill opening. Figure 3 shows the results obtained with the four crude rubbers after 15 minutes' mastication on a cool mill, and for the same rubbers compounded as shown in Table I. The effect of pigmentation,

TABLE I

COMPOUNDS USED IN COMPARISON OF PROCESSING CHARACTERISTICS

	Natural Rubber	GR-S	GR-M	GR-I
Polymer	100	100	100	100
SR black	40	40	30	55
Sulfur	3[a]	2[a]	...	1.5[a]
Light calcined magnesia	...	...	4	...
Zinc oxide	5	5	5[a]	5
Tuads	0.1[a]	...	...	1.0[a]
Captax	0.7[a]	1.5[a]	...	0.5[a]
DPG	...	0.2[a]	...	...
Stearic acid	...	...	...	3.0[a]
Curing time at 298° F, min.	15	30	30	75

[a] These ingredients omitted for determination of relation of extrusion rate to temperature.

generally, is to reduce the shrinkage. Although this is not a precise test, the results do provide a rough comparison of different rubbers which is extremely useful.

Another property of importance in the fabrication of multicomponent products, such as tires and belts, is the property of tackiness. No generally

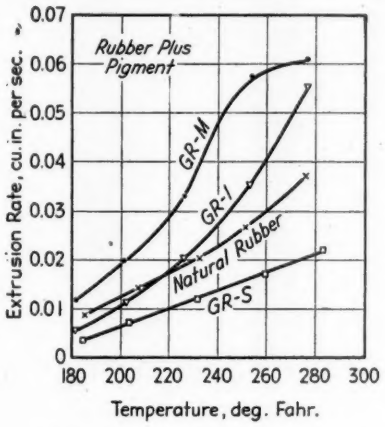

FIG. 4.—Relation between extrusion rate and temperature.

acceptable quantitative measurement has yet been evolved for its evaluation. Tackiness should be distinguished from stickiness. The differentiation which we have found useful is to define tackiness as that property of a rubber or compounded stock which causes two layers of stock, which have been pressed together, to adhere so firmly that separation under force will occur at some point other than at the original two surfaces. If tearing such as this occurs,

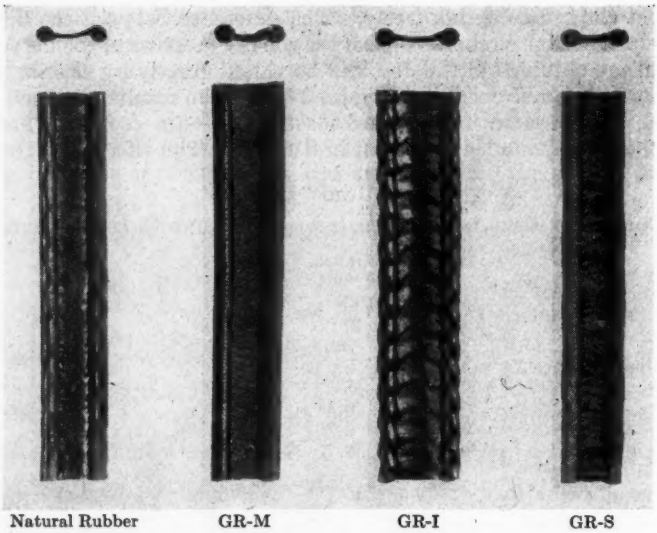

FIG. 5.—Laboratory extruded stocks.

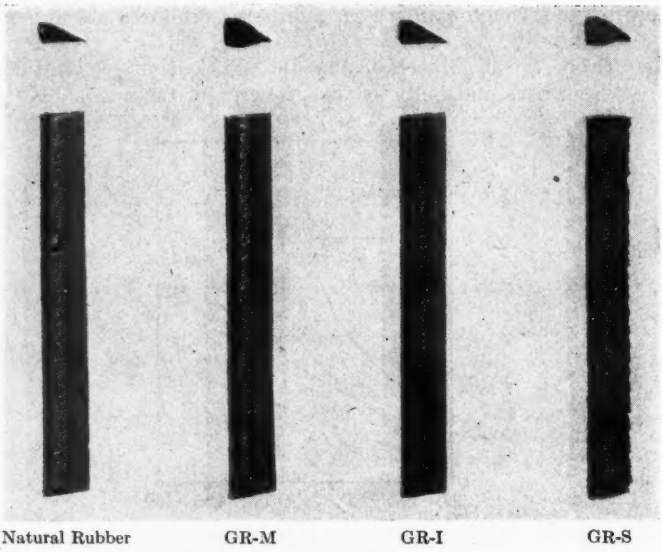

FIG. 6.—Laboratory tubed stocks.

tackiness is rated as excellent. If no tearing occurs, tackiness is rated as poor, while if some tendency to tear is observed the rating may be good or fair, depending on the degree of tearing. Stickiness, on the other hand, results in separation at the surfaces attached, but the separation may take place with varying degrees of force. Based on this differentiation between tackiness and stickiness, natural rubber is rated as having excellent tackiness, GR-M and

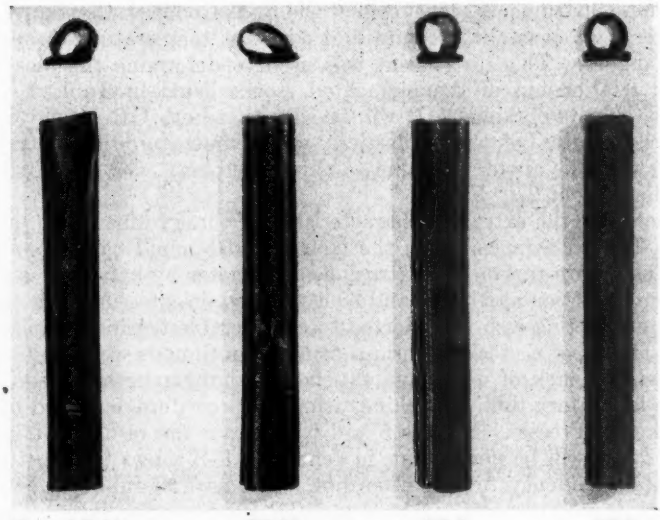

FIG. 7.—Uncured factory extruded stocks.

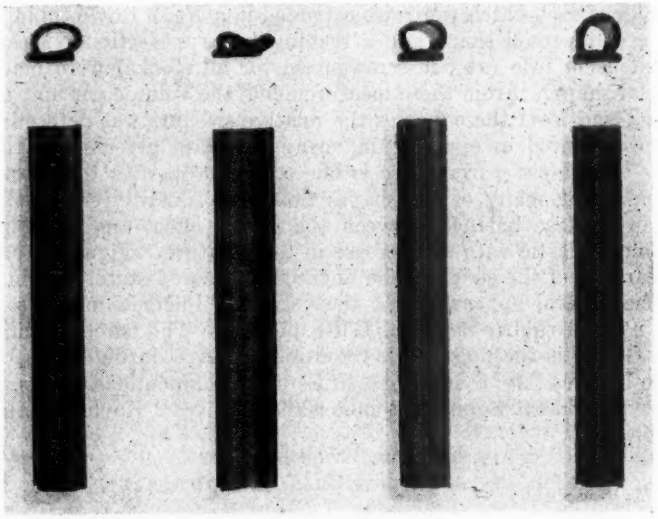

FIG. 8.—Cured factory extruded stocks.

GR-I fair tackiness, and GR-S none. Compounding techniques modify these ratings, in some cases reducing tackiness and in others increasing it. However, it has not yet been possible to attain any considerable degree of true tackiness in GR-S.

A number of plasticity measuring devices are designed to determine the plasticity of rubbers and compounded stocks by extrusion through an orifice.

One of these instruments, developed at the B. F. Goodrich Company[2], extrudes the material at constant pressure and constant temperature through dies of various shapes. This instrument was used to determine the plasticity-temperature relationship of the pigmented stocks listed in Table I. Figure 4 shows the results obtained. It will be seen that both GR-M and GR-I show a relatively greater increase in plasticity with temperature than natural rubber, and that GR-S is about the same as natural rubber. GR-M shows evidence of scorch at about 270° F.

To compare the extrusion characteristics of these rubbers, the same stocks given in Table I were mixed in the factory in 50-pound batches on a 60-inch mill. Tests were run on the extrusion plastometer by extruding a dumbbell-shaped cross section at 212° F, and 20 lbs. per sq. in. pressure. In this section the thin connecting web is subjected to considerable tension during extrusion, and the ability of a stock to form a smooth continuous web in this test indicates desirable lack of nerve and satisfactory hot strength. Tests were also run on a laboratory tubing machine, using the procedure described by Garvey, Whitlock and Freese[3]. Figures 5 and 6 illustrate the results obtained in the two tests. It will be noted that, in general, GR-S shows the most nerve and the greatest tendency to tear when hot, while natural rubber shows the best properties in both respects. GR-M and GR-I are intermediate. The peculiar appearance of the GR-I sample from the extrusion plastometer is thought to be due to alternate sticking and slipping of the stock as it passed through the die.

Samples of each batch were also extruded in a No. 2 Royle tubing machine, in both a commercial shape and a rectangular cross-section. Measurements of the extrusion rate (at one screw-speed for all stocks) were made for the commercial shape. From these measurements the volume per unit length was calculated, and from these figures the relative swelling was determined. The samples were cured in open steam, using the cures given in Table I. The tendency to collapse during cure is one of the properties that must be considered in curing many of the shapes that are ordinarily extruded. This is due to an adverse balance between the curing effect and the tendency to become more plastic with an increase in temperature. Figures 7 and 8 show the appearance of the strips in the uncured and cured state. As in Figures 5 and 6, the general appearance of the various rubbers is in the same order, namely, natural rubber best and GR-S poorest. The cured specimens show that the GR-M is the poorest for retention of shape during cure.

Table II gives the Mooney viscosities of the compounded stocks, the extrusion rates for the extrusion plastometer and the No. 2 Royle tubing machine,

TABLE II

EXTRUSION CHARACTERISTICS

		Laboratory extrusion plastometer		Factory extrusion No. 2 Royle tubing machine		
	Compounded stock—4-min. Mooney SR	Volume extruded per minute, cu. cm.	Relative swell	Volume extruded per minute, cu. cm.	Length extruded per minute, ft.	Relative swell
Natural rubber	29	372	1.0	762	20.7	1.0
GR-S	37	29	0.89	305	8.5	0.97
GR-M	32	46	1.0	622	19.2	0.88
GR-I	36	162	1.09	376	9.3	1.1

and the calculated relative swellings obtained by both methods. The closest correlation is between the Mooney viscosities on the compounded stocks and the factory extrusion rates. The differences between the rates for the extrusion plastometer and the factory tube-machine are doubtless due to the different conditions prevailing in the two tests. In the factory tube-machine the screw speed was held constant, while the temperature and pressure attained in the head depended on the characteristics of the stocks being extruded. In the extrusion plastometer, on the other hand, the pressure and temperature were held constant.

It is generally known that the physical properties of rubber stocks taken from extruded shapes differ from the properties obtained from laboratory press-cured specimens from the same stocks. To see how the four basic rubbers differ in this respect, the stress-strain characteristics for press-cured specimens were compared with those of the open steam-cured rectangular cross-section extruded strip. The results are shown in Table III. It will be seen that the

TABLE III

PHYSICAL PROPERTIES OF PRESS-CURED AND EXTRUDED PRODUCTS

	Press cured products				Extruded products			
	Modulus at 200 per cent elongation	Tensile strength, lbs. per sq. in.	Elongation, per cent	Durometer hardness	Modulus at 200 per cent elongation	Tensile strength, lbs. per sq. in.	Elongation, per cent	Durometer hardness
Natural rubber	420	2850	555	53	720	2750	480	53
GR-S	450	900	300	58	400	790	300	53
GR-M	600	2315	545	65	800	2330	455	58
GR-I	320	1450	665	65	330	1120	575	52

properties are sufficiently different with respect to tensile strength, elongation, or hardness, or all three properties, so that this factor must be considered in setting up specification requirements for extruded products based on laboratory press-cured specimens.

The compounds used in the foregoing comparison were not intended to be suitable for use in extruded goods but were designed to emphasize differences between the basic rubbers in those respects which are important for extrusion. A completely satisfactory comparison of the rubbers is difficult, due to the varying compounding techniques that could be employed to overcome one or another of the difficulties that might be encountered in manufacturing this class of products. The volume loading of pigment was purposely kept low, and is approximately the same for all stocks except the one based on GR-I. A higher loading was used in this case to give a durometer hardness of the cured product in the range of 55 ± 5. This difference results in some advantage to the GR-I in the comparison. Very satisfactory stocks for extrusion purposes can be made from all three of the synthetic rubbers. The deficiencies illustrated in the photographs are intended to show the magnitude of the obstacles which the compounder must overcome for each of the rubbers in producing satisfactory materials.

Certain characteristics of synthetic rubbers impose compounding limitations on each of them which restrict the latitude in their compounding. Compounds combining the properties of extreme softness and high strength cannot be made from GR-S because of the poor quality of its nonreënforced stocks and because of its excessive nerve in lightly pigmented compounds. Soft

stocks of GR-S are made by pigmentation (for reënforcement) plus the use of softeners to lower the hardness. Such stocks in the low hardness range are too thermoplastic for satisfactory extrusion. Also, when channel black, which gives the maximum reënforcement, is used, the stocks have excessive nerve. In general, with GR-S, carbon blacks are the most satisfactory reënforcing pigments, but obviously their use eliminates any possibility of producing light-colored compounds. While GR-M will produce pure-gum stocks of excellent quality, they are excessively nervy and cannot be extruded smoothly without the addition of light loadings of pigments and softeners plus extenders, such as factice, which reduce the quality considerably. Unless special care is exercised in compounding, these soft stocks sag excessively during cure. Pure-gum stocks of GR-I, like those of GR-M, are excessively nervy. Pigmentation plus softeners to give soft stocks results in stocks that are too plastic to retain their shape during cure. This difficulty is aggravated by their slow rates of cure. It appears, therefore, that the principal compounding limitations for all the synthetic rubbers are in stocks in the low hardness range. In the range of 55 durometer hardness and over, all of these synthetic rubbers can be compounded to give very satisfactory extrusions.

There is every possibility that these synthetic rubbers will not remain as they are today. Intensive research is continuing on all the rubbers, and this may result in marked improvement in the crude materials, their processing characteristics, and their compounding limitations. Even without improvements in the crude materials, improved compounding techniques will solve many of the problems that now appear to limit the application of these rubbers.

REFERENCES

[1] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).
[2] Schultz and Bryant, *J. Applied Physics* **15**, 360 (1944).
[3] Garvey, Whitlock and Freese, *Ind. Eng. Chem.* **34**, 1309 (1942).

APPLICATIONS OF ULTRAVIOLET SPECTROGRAPHY A STUDY OF THE TRANSFORMATIONS OF TETRAMETHYLTHIURAM DISULFIDE WHEN IT FUNCTIONS AS A DIRECT VULCANIZING AGENT*

CHARLES DUFRAISSE AND ANDRÉ JARRIJON

In addition to sulfur, which is the most common vulcanizing agent, rubber mixtures usually contain various kinds of accessory ingredients, both inorganic and organic. Among the organic ingredients, some, notably accelerators and antioxidants, are present in relatively small proportions, and these are susceptible to transformation during vulcanization. However, only in rare cases has it been possible to isolate in definite form the products of these transformations, and consequently it is difficult to interpret the part played by these substances during vulcanization.

Since, with few exceptions, each accelerator and each antioxidant has its own characteristic absorption spectrum in the ultraviolet region, spectrography constitutes in general an important method for following the behavior of accelerators and antioxidants. This method has been demonstrated by Dufraisse and Houpillart[1], who have developed a special technique[2] for obtaining ultraviolet absorption spectra and examining them, frequently with interesting conclusions to be drawn from such analyses.

The method was first applied to a simple case, the determination of antioxidants[3]. It was proved in this way that these substances remain unchanged in vulcanized mixtures. From this preliminary study, attention was turned to a more complicated problem, that of tetramethylthiuram disulfide. This compound was originally used as an accelerator, but it was found later that it serves as a direct vulcanizing agent in the absence of elemental sulfur itself. Several different explanations have been offered regarding the action of this compound in this way.

As a result of the work of Bruni[4], the belief has been held by many that tetramethylthiuram disulfide is transformed into tetramethylthiuram monosulfide, with liberation of one atom of sulfur from each molecule of the disulfide. On the other hand, it has been assumed by others that simple pyrogenic decomposition of tetramethylthiuram disulfide, with liberation of tetramethylthiourea, takes place during vulcanization. Finally, two investigators, Shimada[5] and Shepard[6], have reported independently that, based on color reactions, they were able to detect the presence of zinc dimethyldithiocarbamate.

In view of this, the present authors have attempted, by the application of the methods of ultraviolet spectrography, to identify the transformations which tetramethylthiuram disulfide undergoes during vulcanization.

The mixture used in the experiments had the following composition: pale

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 215, pages 181–182, August 18, 1942.

crepe 100, tetramethylthiuram disulfide 3, and zinc oxide 2. It was vulcanized for 30 minutes at 125° C. Extraction of the vulcanizate by acetone gave 3.5 per cent by weight of extract, the spectrum of which was then obtained.

This spectrum was characteristic, and showed maximum absorption points at wave lengths of 2800 and 2600 Å. U. Such a spectrum is not that of tetramethylthiuram disulfide, nor that of tetramethylthiuram monosulfide, nor finally that of tetramethylthiourea, but instead is identical with that of zinc dimethyldithiocarbamate.

According to this evaluation by the spectrometric method, two-thirds of the tetramethylthiuram disulfide originally added is transformed into zinc dimethyldithiocarbamate.

This extensive transformation of tetramethylthiuram disulfide is, without any doubt, related in some way to its power to bring about vulcanization. Chemical work is in progress to obtain more precise information about this phenomenon, and to try to explain the nature of the effects of this transformation on the rubber.

REFERENCES

[1] Dufraisse and Houpillart, *Rev. gén. caoutchouc* **16**, 44 (1939).
[2] Dufraisse and Houpillart, *Rev. Opt. Theor. Instr.* **16**, 321 (1937).
[3] Jarrijon, *Rev. gén. caoutchouc* **18**, 217 (1941).
[4] Bruni, *India-Rubber J.* **62**, 89 (1921).
[5] Shimada, *J. Soc. Rubber Ind. Japan* **10**, 431 (1937); RUBBER CHEM. TECH. **11**, 535 (1938).
[6] Shepard, *Ind. Eng. Chem.* **26**, 1200 (1934).

CELLULAR RUBBERS *

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The nomenclature of the rubber products which are to be discussed in this paper has not been too exact. There are patents entitled froth rubber, expanded rubber, and cellular rubber, all of which refer to the same product. One patent named cellular rubber describes a product which is similar to that of another patent called microporous rubber. Sponge rubber, porous rubber, foam rubber, and other names have been used rather loosely, and manufacturers themselves have not been in complete agreement as to the correct names for some of these products. In most groups of products there is considerable similarity between the different members of the group, but this is not true in this family of cellular rubbers; for example, a microporous hard-rubber battery separator is quite dissimilar to a latex foam rubber cushion but they do have one thing in common—they are both cellular, that is, consist of cells, which are defined as small hollow receptacles. The first problem then is to classify and define the various products included in the cellular rubber family. In this paper the term rubber has been used to include both natural rubber and synthetic types, except where one or the other is specifically mentioned.

CLASSIFICATION

Cellular rubbers have been divided according to cell structure of the finished products into three classes: Class 1, multicellular rubbers, with open-cell structure; Class 2, unicellular rubbers, with closed-cell structure; and Class 3, microcellular rubbers, with cells too small to be readily visible to the naked eye. Related products are impregnated fibers and cellular products made from materials other than rubber. Many of the products are made both in soft and in hard (ebonite) rubber. Multicellular rubbers have been divided into sponge rubbers and latex-foam rubbers, and microcellular rubbers have been divided into microporous and multiporous sheet rubbers.

The words "sponge rubbers" to cover the entire group of products have been avoided, because by definition a sponge is a material remarkable for its power of absorbing water. Cellular rubbers with an open-cell structure absorb water and those made from slab rubbers are known as sponge rubbers. Their cell structure is interconnecting or intercommunicating in the finished products. The word finished is emphasized because some of the products of this group have a closed-cell structure in earlier stages of their manufacture. Articles which are made to compete with natural sea-sponges, such as artificial bath sponges, will be referred to as rubber sponges—the order of the two words is reversed to identify the one particular product. Products of Class 1 made from rubber latices will be designated as latex-foam rubbers. Products of the closed-cell type certainly should not be classified as sponge rubbers because by

* This is one of thirteen papers comprising a "Symposium on the applications of synthetic rubbers" at the 1944 Spring Meeting of the American Society for Testing Materials, held at Cincinnati, Ohio, March 2, 1944. It is reprinted here from the Society's booklet containing the complete symposium.

their very nature they are resistant to the absorption of water. Manufacturers of products with closed-cell structures have objected to the word "sponge" being used in connection with their product, which is not only resistant to absorption of water, but is actually used in water for floats and buoys. Products of Class 2 will, therefore, be referred to as expanded rubbers—the name used in the patents of Marshall[1], Denton[2], and Roberts[3]. The name aptly describes what happens at one stage of the manufacturing process when rapid expansion of the mass takes place. While the name cellular has heretofore been used only for products of Class 2, all three classes are certainly cellular; in fact, this is the only word which seems to be descriptive of the entire group. Cellular, without the modifier "closed-cell" does not accurately differentiate the products of Class 2 from the other classes. The name "chemically blown", which has been used to identify the sponge rubbers included in the open-cell group, is no longer a distinguishing characteristic of this group alone, because much of the production of the closed-cell group, all of which was formerly made by externally gassing the compound, is now made by the use of chemical blowing agents incorporated into the compound.

The suggested classification is shown in Table I.

TABLE I

CLASSIFICATION OF CELLULAR RUBBERS AND RELATED PRODUCTS

Class 1.—*Multicellular* (open-cell structure):
- Sponge rubbers, made from slab rubbers
  - (*1*) Press cured
  - (*2*) Steam cured
  - (*3*) Oven cured
- Latex foam rubbers, made from rubber latices
  - (*1*) Mechanically foamed latex
  - (*2*) Blown latex
  - (*3*) Miscellaneous processes

Class 2.—*Unicellular* (closed-cell structure):
- Expanded rubbers, made from slab rubbers
  - (*1*) By external gassing
  - (*2*) By incorporating gas forming ingredients in the compound

Class 3.—*Microcellular* (cells not readily visible to the naked eye):
- Microporous rubbers, made from rubber latices
- Multiporous sheet rubbers, made from rubber latices

Class 4.—*Related products:*
- Impregnated fibers (reticulated or network structure)
- Products made from materials other than rubber (various structures)
  - (*1*) Rigid and nonrigid plastics
  - (*2*) Cellulose sponges
  - (*3*) Foams made from glass
  - (*4*) Felt products

PROCESSES FOR MAKING CELLULAR RUBBERS

Sponge rubbers are made by incorporating into plasticized slab rubbers an inflating agent such as sodium bicarbonate, together with proper vulcanizing ingredients, softeners, fillers, and age-resisters. During the vulcanization process a gas is produced which expands the mass. The bulk of this type of sponge rubber is press-cured in moulds, although a closely related type is cured in loaves or rods, either in hot-air ovens or steam autoclaves. This latter type is the one from which such products as rubber sponges are made, and is believed to be one of the earliest cellular rubber products. Quite a bit of waste results, due to cutting up the cured loaf, which except for size somewhat resembles a

loaf of bread. Sponge rubber manufacturing is in some respects similar to the baking industry. It is said that the first rubber sponges were made in Russia, and were the result of an observation made after a rubber cement plant had been destroyed by fire. Sponge rubbers have been divided into three groups, depending on the method of vulcanization. These three methods of vulcanizing are used to produce entirely different finished products. This is not true of solid rubber products, nor is it true of other types of cellular rubbers, as, for example, with latex-foam rubber very little difference in the structure of the end product results if it is vulcanized in steam, hot-air ovens, or hot water.

One method of producing sponge rubbers by externally gassing the compound with carbon dioxide[4] is illustrated graphically in Figure 1. The uncured

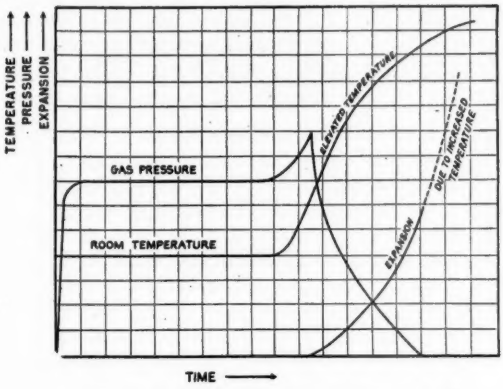

FIG. 1.—Carbon dioxide, low-pressure method.

stock is placed either directly or in a ventilated mould in a steam jacketed autoclave, which is charged with carbon dioxide gas at room temperature. After a gassing period the temperature of the inside chamber is raised by admitting steam into the outer chamber of the autoclave. The heat causes an increase in the pressure of the gas in the autoclave. After the stock has been sufficiently warmed and saturated with gas, the pressure in the inner chamber is slowly released through an orifice while the heating is continued until vulcanization is complete. The expansion of the mass is due to the decrease in external pressure and to the continued rise in temperature, which increases the internal pressure of the trapped gas.

Many sponge rubber products must be put through mangles or wringer rolls to break up the closed cells and make them intercommunicating. An interesting story was told by Willis and Felix[5], who years ago, while working on the problem of making rubber sponges, passed through a laboratory mill some of the rubber sponge trials which they had previously made and discarded because they had collapsed and shrunk. They were surprised when the cells were broken and filled with air and the flat shriveled tubes developed into good rubber sponges. This was an important discovery, and the method of breaking up closed cells mechanically by passing the sponge rubber through tight wringer rolls is still a standard practice.

Latex sponge rubbers are ordinarily made by whipping air into rubber latices[6]. The process is similar in some respects to beating up egg whites or whipping cream in a household mixer. After the foam is made, a delayed

coagulant is added and the foam poured into moulds, which are completely filled. After gelling has taken place, the moulds are placed in water, steam, or hot-air ovens, and the foam is vulcanized. Another process consists of adding cooled liquid butane in the form of an emulsion to the latex, after which foaming is accomplished by rolling the mixture in drums which are partly submerged in warm water. The remainder of the process is similar to that of the first method mentioned. Many other processes such as freezing latex[7], using crushed ice particles to form the cells, or using weak blowing agents in conjunction with a vacuum[8] to facilitate sponging, have been used.

Expanded rubbers with a closed-cell structure are made by subjecting the compound to a gas such as nitrogen under high pressures[9]. Under these conditions a certain amount of gas dissolves in the compound. At the end of a semicuring period the gas pressure is lowered, causing the mass to expand rapidly, and myriads of individual nonconnecting gastight cells are formed. The semi-cured pieces are then given a final cure. This process is illustrated graphically in Figure 2. In this process the uncured mass is placed in a high-

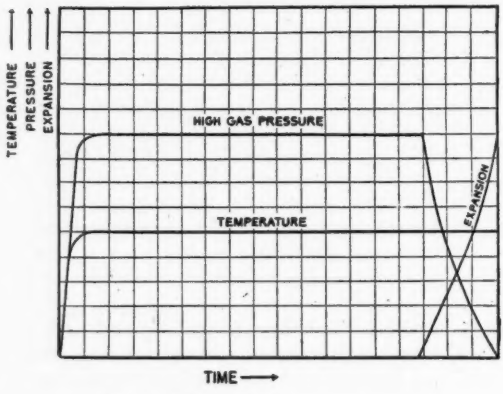

FIG. 2.—Nitrogen, high-pressure method.

pressure autoclave and subjected to a pressure of nitrogen of approximately 4500 lbs. per sq. in. The temperature is maintained constant throughout the cycle, and at the end of a semicuring period the gas pressure is rapidly reduced, causing the mass to expand. The gassed semicured pieces are then given a final cure. This product is also being made by incorporating a gas-inflating material in the compound, semicuring in a first mould similar to the manner of curing solid rubber articles, removing from the mould, at which time considerable expansion takes place, and then giving the product a final cure in a second mould which is slightly larger than the expanded semicured piece. The two-stage process is necessary to get a product with a completely closed-cell structure.

Microcellular rubbers have been classed as either microporous or multiporous to distinguish between two distinct types. Microporous rubbers[10] are made by curing wet coagulums under conditions which trap the water in the product during vulcanization. The cells in the finished product are microscopic in size. Microporous rubber could be included with the open-cell type of cellular rubbers but differs from them mainly in cell size. Multiporous products[11], consisting of porous sheets made from latices, derive their porous

characteristics from many minute and uniformly spaced holes that extend perpendicularly through the sheet. They are made by spreading latex on a pitted blanket. The latex completely covers all the pits in the blanket surface but does not run down into them. Thus air is trapped in each little pit. Heat is then applied to the under surface of the blanket by a steam platen and as the belt becomes hot the air in the pits expands, blowing little bubbles into the film of latex. When the bubbles burst, small holes are left in the film of rubber, corresponding in size and number to the pits in the blanket surface. The term "expanded" is used also in connection with this product, and represents the material obtained by elongating the uncured sheet and then vulcanizing. This, of course, changes the shape of the pores.

A few related products containing little or no rubber may be mentioned because they are similar to the cellular rubbers, and in some cases compete with them. Products with a reticulated network structure are made by impregnating hair, glass fibers, steel wool, or other materials with binders such as rubber latices or reclaimed rubber dispersions. These products are sometimes shaped into definite configurations. They should not be classified with cellular rubbers because the amount of rubber used in their manufacture is small compared with the amount of other materials used. Cellular rigid products are currently being made from thermoplastic resins such as polystyrene, cellulose acetate, and others, by mixing the resin with a blowing agent and extruding the material out of a hot die. It seems probable that there will be considerable future development in this field. Multicellular products of the open-cell type are also being produced from plasticized vinyl chloride, a nonrigid plastic. Artificial sponges are made from cellulose[12] by incorporating sodium sulfate crystals into viscose, placing the mixture in a coagulating bath, and precipitating the cellulose. The blocks so formed are leached with warm water to remove the sodium sulfate crystals, which leave corresponding cavities. These sponges, like sea sponges, are remarkable for their power of absorbing water, becoming soft when wet without losing their toughness. Cell sizes vary according to the sizes of the crystals used. Foamed glass is a new product that is structurally strong, is a good insulator, and is fireproof.

The remainder of this paper deals only with the products classified as sponge rubbers, latex-foam rubbers, and expanded rubbers, as these constitute by far the largest portion of cellular rubber production.

SPONGE RUBBER THEORIES

In looking over the records of an early experimenter who was working on the problem of making rubber sponges, an entry was found in his notebook that he had discovered how to make the improved product by allowing the uncured stock to age or mature before curing; he recommended that the maturing period be ninety days. Since that time considerable progress has been made, but there is still much to be learned about cellular rubbers. One company is attacking the problem through the establishment of a research foundation at one of the larger universities. In the manufacture of sponge rubbers the following factors are important. They are based largely on work done with natural rubber.

UNCURED MASS MUST BE PLASTIC

The mass must be sufficiently plastic to be expanded by the gas or vapor pressure developed within the compound. Otherwise, the required cells will not be formed.

RATE OF BLOW AND RATE OF CURE MUST BE BALANCED

Blowing must not take place too early during the cure for otherwise the cell walls collapse and the gas escapes, nor should it take place too late during the cure because it will not then be able to expand the partially cured stock. This fact is easily demonstrated by mixing a blowing agent into a well-plasticized compound which does not contain any vulcanizing agents. During the heating process only slight expansion of the mass takes place, due to loss of gas through the material, which fails to decrease in plasticity and increase in elasticity sufficiently to entrap the gases which are generated. With certain synthetic rubbers the required change of consistency for proper blowing takes place by increased polymerization due to the heating rather than by vulcanization as with natural rubber, but the results are similar. The various possible conditions of balance between the rate of cure and rate of blow are illustrated graphically in Figure 3. Under (*a*) is shown a medium-fast curing sponge rubber compound with a balanced rate of blow. These conditions result in a good product, with medium sized cells and maximum amount of expansion. In (*b*) the rate of blow lags behind the rate of cure, and a product results with a good skin, small cells, but not much expansion. In (*c*) the rate of cure lags behind the rate of blow, and a product results which has a thin porous skin, large uneven cells and a medium amount of expansion. In (*d*) a faster curing compound is illustrated. To obtain the best product in this case, the faster curing compound must be balanced with a faster blowing agent. Ammonium bicarbonate might be substituted for the sodium bicarbonate and stearic acid which were used in the hypothetical case represented by (*d*). In (*e*) we have represented a slower curing compound which calls for a blowing agent with a slower rate of reaction, such as sodium bicarbonate without an acid. In (*f*) is shown the rate of blow obtained by the use of an auxiliary blowing agent, and in (*g*) a rate of cure obtained by using a delayed-action type of accelerator

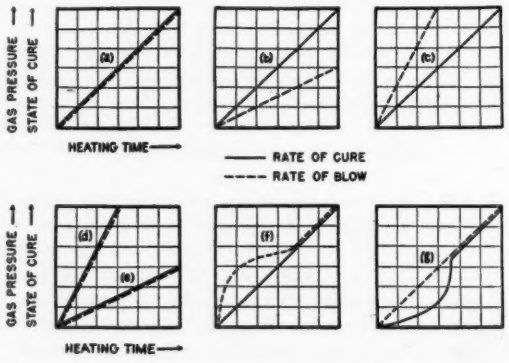

FIG. 3.—Relation of rate of cure to rate of blow.

or by adding a retarder to the compound. Figure 3 (*g*), we believe, represents the best conditions. Figure 3 (*f*) is, of course, similar. Balance between rate of cure and rate of blow can sometimes be changed by raising or lowering the temperature of cure, which will affect the rate of blow differently. In practice it is sometimes difficult to distinguish whether the cure is too slow or the blow

is too fast, or the opposite, as both sets of conditions result in a cured product of similar appearance.

Cells are formed during the early part of the curing period, and for this reason the initial part of the curing (or decrease in plasticity) curve is very important in the manufacture of sponge rubbers. Figure 4 shows theoretical

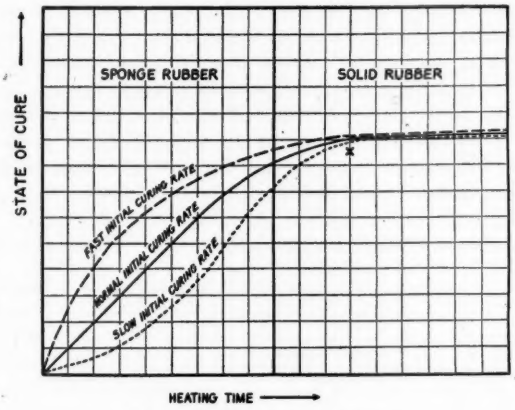

FIG. 4.—Theoretical curing curves.

curing curves for three possible variations obtained with the same recipe. Since the curves all meet at a point which can be considered as the proper cure, all three stocks would ordinarily be satisfactory for solid moulded products. However, the variation in initial rate of cure causes considerable variation in cell structure of cured sponge rubber. The initial rate of cure is possibly more important in sponge manufacture than in the manufacture of any other type of rubber goods. It is exceedingly hard to control, for it is influenced greatly by changes in plasticity of the rubber, and it varies with different lots of rubber and with different shipments of supposedly inert pigments.

INTERNAL PRESSURE MUST EXCEED EXTERNAL PRESSURE

In an ordinary press-cured sponge rubber mix, the pressure developed within the mass during cure exceeds the external atmospheric pressure. In one process a weak blowing agent is used, and the expansion is aided by reducing the external pressure by a vacuum. Articles which are cured in open steam usually contain water, on the theory that the water will generate, at the curing temperature, an internal pressure which will exactly counterbalance the external steam pressure. The blowing is accomplished with a secondary blowing agent which increases the internal pressure above that of the external steam pressure. Sponging can be accomplished either by lowering the external pressure or by raising the temperature, which increases the internal pressure.

RATE OF HEAT TRANSFER IS IMPORTANT

An important factor in sponge rubber manufacture is the rate of heat transfer. Many of the difficulties of sponge rubber manufacture can be traced to the slow transfer of heat into the mix because of the low heat conductivity of rubber and the additional insulation due to the premature blowing of the

outside layers of the sponge rubber. If a roll of stock is put in a vulcanizer, the steam heats the outer surface, which becomes porous and insulates the interior of the stock, resulting in different sizes of cells from center to outside. A stock which makes a good sponge rubber when sheeted out 0.5 inch thick and cured in open steam, often does not make a satisfactory sponge rubber if an attempt is made to make a thicker sponge using a 1-inch thick stock preparation. Press-cured sponge rubber slabs often have the top edges rounded, due to heat being transferred into sides of stock from three directions while the center of the stock is only being heated from top and bottom. Articles such as sponge rubber balls sometimes have a loose bottom layer, due to premature blowing and curing of that part of the biscuit which is in direct contact with the hot mould. This takes place before the top and outer parts of the biscuit are heated to the blowing temperature. To obtain better heat transfer into compounds which are vulcanized in hot air ovens, it is sometimes advantageous to saturate the air with water vapor to increase its conductivity. Superheated steam at atmospheric pressure also has been used. Thermal conductivities of

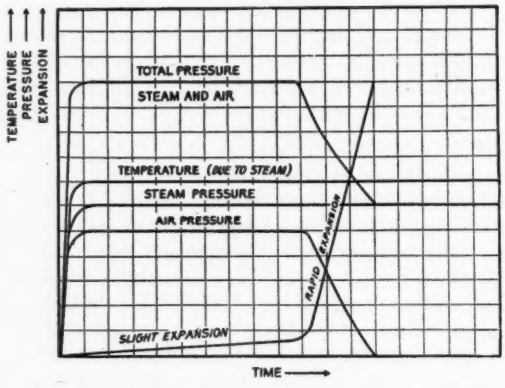

FIG. 5.—Lindemann method of curing sponge rubber.

the various polymers differ, but in general are greater for the synthetic rubbers than for natural rubber.

To overcome these difficulties of heat transfer, a process of making sponge rubber was developed in Europe which consisted of heating the mix in a steam-jacketed heater filled with water at the vulcanizing temperature and at the same time applying to the water a pressure sufficiently high to prevent expansion of the rubber mix until it had been evenly heated throughout. The pressure was then reduced while maintaining the water at the vulcanizing temperature and the gas-producing ingredients caused the mass to expand rapidly, which resulted in sponge rubber with a uniform distribution of cells throughout its mass. Vulcanization took place in two stages, the warming up and semicuring period and the final vulcanization period. This method was improved by Lindemann[13], who heated the mass in a chamber containing a mixture of a gas introduced at a substantial pressure with steam at the proper vulcanizing temperature. This provided in the chamber the proper vulcanizing temperature and a pressure practically sufficient to prevent expansion of the mix under the influence of the gas-producing ingredients. The process is illustrated graphically in Figure 5. After the mass was uniformly heated

throughout and partially vulcanized, the pressure was reduced to permit expansion of the mass under the influence of the gas-forming ingredients. The proper vulcanizing temperature was maintained by the steam until vulcanization of the sponge rubber was complete.

PERMEABILITY OF RUBBERS TO VARIOUS GASES IS IMPORTANT

This is important in the formation of the cells in sponge rubbers, but it is possibly more important in the field of unicellular rubbers. The soft expanded rubbers made from polymers which have the least permeability to the trapped gases retain their usefulness for the longest period of time. The solubility of the gases in the polymers is important. In latex work, the solubility of the gases in the liquid phase is also important.

PRESENT STATUS OF CELLULAR RUBBERS

ACKNOWLEDGMENT

The information presented in this paper and especially in this section is largely the result of a survey of the cellular rubber industries, and would not have been possible except for the coöperation of a large number of persons. Their considerable assistance is acknowledged with thanks. It must be remembered that different results can be expected with differences in compounding technique; also that the field is new and ideas are rapidly changing. The statements made are based on general opinions and not on exact experimental data.

SPONGE RUBBERS

Sponge rubber products are being made today from almost all of the various types of synthetic rubbers. The choice of the synthetic rubber to be used for a particular sponge rubber application depends, as in the case of other synthetic rubber items, on whether or not any special properties are desired in the finished product. General purpose items are usually made from either Buna-S (GR-S) or from Neoprene-GN (GR-M). When sufficient quantities or Butyl (GR-I) are available, it will no doubt also be used for some of these applications. If a special property or a combination of special properties such as heat resistance, low temperature compressibility, or resistance to oils is desired, then one particular synthetic rubber or a combination of two or more synthetic rubbers is employed to make that item.

Oil resistance of sponge rubbers, unless covered with an added solid synthetic rubber skin, is not so great as the resistance of the corresponding polymer when moulded solid. This is, of course, due to the thin skin and cell walls of the sponge rubber. However, although the volume change is higher than on solid rubbers, the pieces retain considerable strength, and do not disintegrate in petroleum base oils, as do sponge rubbers made from natural rubber.

Low-temperature compressibility is becoming increasingly more important in wartime sponge rubber applications. This type of product finds many uses in high altitude planes of today. It should be pointed out that low-temperature compressibility and low-temperature flexibility are not synonymous in sponge rubber. A sponge rubber may be very flexible at subzero temperatures, yet be very difficult to compress. Likewise, a synthetic solid rubber compound that is flexible at $-50°$ F, if converted into a sponge rubber compound, will probably not be compressible below $-20°$ F without application of tremendous

loads. Hard synthetic (ebonite) sponge rubber is being made from GR-S and Buna-N. These hard sponge rubber products are very similar to those made from natural rubber and in some properties, notably tensile and impact strength, are even superior. These hard sponge rubber products find many uses as floats, insulation materials, etc.

GR-S is being used to make various general purpose sponge rubber items which were formerly made from natural rubber. Some of these are: strip and sheet sponge, moulded car cushions, eye goggles, eye buffers for bomb sights and aiming devices, ramp-gate gaskets for landing barges, cowl ventilator gaskets, sealing strips, and a variety of other items. Since GR-S is an oil-soluble type of synthetic rubber, it is not oil resistant. It can be compounded to be more easily compressible at subzero temperatures than any other synthetic rubber, and closely resembles natural rubber in this respect. It can likewise be compounded to have good resistance to heat aging. One company reported that the difficulty of calendering thick sheets of GR-S stock had limited their production for the time being to 0.25-inch thick finished sponge rubber sheets.

Buna-N is ordinarily used only in sponge rubber applications where extremely low swelling in petroleum base oils is necessary. Products made from Buna-N consequently find many uses in the aircraft, tank, and automotive industries, as oil seals, gaskets, etc. Unlike GR-S sponge rubber, this type does not possess good low-temperature compressibility.

Sponge rubber made from Neoprene-GN was originally used only where medium low swelling in petroleum base oils was necessary. However, since the advent of the war, Neoprene-GN (GR-M) has been used to make sponge rubber for a wide variety of general purpose uses. These sponge items closely resemble those made from natural rubber. GR-M sponge rubber possesses one other property that finds some applications; it does not support combustion. Ordinarily it does not have very good low-temperature compressibility. The sunlight resistance of all types of Neoprene sponge rubber is very important. In normal times considerable Neoprene sponge rubber would probably be used for channel rubber, gas tank gaskets, and cowl ventilator gaskets. The use of Neoprene in these applications might eliminate the necessity for the application of an added solid skin to the sponge rubber. The sunlight and oil resistance of Neoprene sponge rubber makes it ideal for use as goggle frames, sweat bands, ear phones, and other uses where such a combination of properties is required. Most manufacturers now find that the production of Neoprene sponge rubber is easier to control than the production of natural sponge rubber. One reason for this is that Neoprene may be readily plasticized chemically to any desired plasticity.

Neoprene-FR was developed for freeze-resistant applications, and is being used widely in the aircraft industry in many moulded and extruded shapes. The supply has been limited by these many uses and, consequently, not much sponge rubber has been made from it. Sponge rubber items made from Neoprene-FR closely resemble those made from natural rubber. The low-temperature compressibility of this sponge rubber is not so good as that of GR-S, but is much superior to that of GR-M and Buna-N. Neoprene-FR sponge rubber is somewhat oil-resistant, but does not approach Buna-N or GR-M in this respect. Many postwar uses will be found for this type of sponge rubber.

Due to the limited supply of Butyl (GR-I) only a small amount of work has been done to make Butyl sponge rubber. The sponge rubbers which have been

made have had fairly good properties. No doubt uses will be found for this type of sponge rubber when Butyl becomes more available.

Cellular products having fairly good resistance to paraffin-base oils, excellent resistance to almost all acids and corrosives, excellent sunlight resistance, and excellent flame resistance, have been made from plasticized vinyl chlorides. However, these sponge rubbers are thermoplastic, and their use should be limited to temperatures between 0° and 140° F.

While it is possible to vulcanize the Thiokols to porous, spongy masses, the nature of these materials is such that they do not make satisfactory sponge rubbers. This is tied up to a large extent with the cold-flow characteristics of the Thiokols that have been produced heretofore. A new Thiokol that is capable of being vulcanized so as to greatly diminish the thermoplastic characteristics of the vulcanizate will probably make satisfactory sponge rubber.

The comparative properties of sponge rubbers made from the various rubbers are shown in Table II.

TABLE II

COMPARATIVE PROPERTIES OF SPONGE RUBBERS
(Proper compounding for desired properties is assumed)

Base material	General characteristics	Heat resistance	Low-temperature compressibility	Swelling in petroleum base oils	Flame resistance	Compression-set
Natural rubber	Good	Good	Good	High	Burns	Excellent
Buna-S (GR-S)	Good	Good	Good	High	Burns	Good
Buna-N	Good	Good	Poor	Low	Burns	Good
Neoprene-GN (GR-M)	Good	Good	Poor	Medium	Does not burn	Good
Neoprene-FR	Good	Good	Good	Medium	Burns	Excellent
Butyl (GR-I)	Good	Fair	Fair	High	Burns	Fair
Plasticized vinyl chlorides	Good	Poor[a]	Poor	Medium	Does not burn	Fair

[a] This is a thermoplastic, and should not be used at temperatures above 140° F.

Since the volume compressibility of solid rubbers is extremely low, they cannot be used successfully in compression unless space is provided for lateral expansion. The property of being highly compressible accounts for many of the uses of sponge rubbers. This class of the cellular rubber family is used for seals, insulators, fillers, cushions, vibration absorbers, etc.

LATEX-FOAM RUBBERS

In this field good results have been obtained with Neoprene-GN (GR-M) latex. Physical properties of the cured sponge rubber vary somewhat from lot to lot, but in general it may be said of Neoprene latex-foam rubber that the aging properties, as measured by the oxygen bomb, are excellent, and resistance to oil is superior to that of products made from natural rubber latex. The unfavorable properties of Neoprene latex-foam rubber are shrinkage, which is approximately twice that of natural rubber latex-foam rubber, poor freeze resistance in the unplasticized state, and only slight improvement when freeze-resistant plasticizers are added. The shrinkage mentioned is a manufacturing problem, and in no way affects the finished product. It is believed that shrinkage can be reduced by using more concentrated Neoprene latex. Permanent set is greater than in natural-rubber latex sponge, but it is believed that this can be improved. Cold-resistant latex-foam rubber shows a greater permanent set than the unplasticized material. Difficulties have been encountered trying to produce latex foam rubbers from either Buna-S (GR-S) or

Buna-N latices. In addition to the troubles caused by low concentration, additional difficulties are due to the instability of some latices toward mechanical agitation, the adverse effects of some emulsifying agents on foam stability, and the excessive amount of soap which adversely affects coagulation. These difficulties will no doubt be overcome in a short time, or possibly they have already been overcome. Another company reports that latex-foam rubber has been made from Perbunan latex. The flame resistance of all types of Neoprene latex-foam rubber is especially important in the case of truck cushions, car and bus upholstery, and airplane cushions, where serious accidents have occurred, due to the flammability of latex-foam rubber made from natural rubber.

The porosity of latex-foam rubbers permits the free passage of air through them, thus providing the ventilation and cooling necessary when the products are used for pads, cushions, mattresses, and similar articles.

EXPANDED RUBBERS

In the field of expanded rubbers, good products have been made from Butyl (GR-I), Neoprene-GN (GR-M), Buna-N, and Buna-S (GR-S). In this field, it would seem that GR-M and GR-I give the best soft expanded rubber, due to their relative impermeability to gases. The end use determines to a great extent the synthetic rubber which is preferred. Where resistance to aviation fuels is required, Buna-N is used. For water resistance, GR-I, GR-S, and Buna-N are satisfactory, but GR-M is poor. The hard (ebonite) type of expanded rubber when made from Buna-N has a softening or bending point of 250° F; a corresponding product made from natural rubber softens almost 100° F lower.

Expanded soft rubbers act as admirable cushioning material, since each cell encases a small amount of gas which must be deformed to absorb shock. The resistance of literally millions of these cells to deformation makes this type of material particularly good for cushioning and resistance to impact. These products are apt to lose gas pressure and become distorted if used in compression. The hard-rubber expanded product is extremely light in weight, yet has high tensile strength, and is strong and durable. Likewise, each of the individual cells offers maximum insulation value, as each cell is isolated from every other cell. Hard rubber floats are made from cell-tight expanded rubber. When these floats are pierced by a bullet, only a small hole is made, and a correspondingly small amount of buoyancy is lost, whereas a bullet hole through a hollow metal float is apt to completely destroy its usefulness.

SPECIFICATIONS

During the past year specifications have been written for cellular rubbers. They are modeled after the A.S.T.M. Tentative Specifications for Rubber and Synthetic Rubber Compounds for Automotive and Aeronautical Applications[14], which are intended for solid rubber products and were developed by Technical Committee A on Automotive Rubber, of the A.S.T.M. Committee D-11 on Rubber Products, functioning under the joint sponsorship of the American Society for Testing Materials and the Society of Automotive Engineers. The work on cellular rubber specifications was done at the request of the United States Army Ordnance Department by a committee composed of producers and consumers of cellular rubber products. For many years cellular rubbers

have been evaluated mainly on an apparent specific-gravity basis. In the new specifications, this requirement, together with those for tensile strength and elongation, has been eliminated and, instead, load-deflection values have been substituted. Most multicellular rubbers are used in compression, and it is believed that designers and engineers will appreciate this change. Tests for oven aging, oil resistance, cold resistance, compression-set, water absorption, and flexing have been included in the specification, as these seem to have important relations to performance characteristics.

Table III shows a part of one of the tables of the specifications for cellular rubbers. In the specifications, cellular rubbers were divided into two types,

TABLE III

PHYSICAL REQUIREMENTS—CELLULAR RUBBERS, TYPE S, CLASS SB, OIL RESISTANT—LOW SWELLING

	Basic requirements		Requirements added by suffix letters				
			Suffix A	Suffix B	Suffix F	Suffix H	Suffix L
PN RU EM FB IE XR	Load deflection psi 25% deflection	Oil aged 22 hr. ×158° F Vol. change 160° F, AP oil	Oven aged 7 days ×158° F Chg. from orig. load-defl. or indent. values	Comp.-Set 22 hr. ×158° F Deflection 50% 25%	Cold test Change from original deflection values	Flexing test Comp.-set	Water absorption
	(limits)	(limits)	(limits)	(maximum)	(maximum)	(maximum)	(maximum)
	Sponge rubbers						
SB 11	2– 5	−25 +10	±20%	15% —	50%		
SB 12	5– 9	−25 +10	±20%	20% —	50%		
SB 13	9–13	−25 +10	±20%	25% —	50%		
SB 14	13–17	−25 +10	±20%	— 15%	50%		
SB 15	17–24	−25 +10	±20%	— 20%	50%		

those for which no specific resistance to oils is required and those which must be oil-resistant, and subdivided into four classes, each of which includes sponge rubbers, latex-foam rubbers, and expanded rubbers. Table III is for cellular rubbers, Type S, Class SB, oil resistant-low swelling. The left-hand digit of the number identifies the material as sponge rubber, and the digit to the right indicates the degree of firmness, the softer grades being identified with the lower numbers. SB 11, for example, specifies a sponge rubber with a load-deflection value of 2 to 5 psi, and a volume change on oil immersion of −25 to +10 per cent. SB 11, with the added suffix letters A, B, and F, specifies that in addition to the basic requirements, an oven aging test, a compression-set test, and a cold test are required.

CONCLUSIONS

This paper has presented a report on the progress which has been made in the cellular rubber field during the past several years; now a few words about the future. It is said that Russia has seventeen kinds of Buna-S. At present the United States has only one kind, namely, GR-S. Of course, this country does have several types of Buna-N and several types of Neoprene. Possibly the day will come when there will be available one or more types of both solid and liquid synthetic rubbers made specifically for the manufacture of cellular rubber products. In the past, many production difficulties in this field have been due to variation in the plasticity and in the rate of cure of different lots of natural rubbers, and to variation in the stability and rate of cure of different shipments of natural rubber latices. These difficulties may well be overcome in the synthetic rubbers of tomorrow.

REFERENCES

[1] Marshall, U. S. patent 1,551,110 (Aug. 25, 1925).
[2] Denton, U. S. patent 1,905,269 (Apr. 25, 1933).
[3] Roberts, U. S. patent 2,086,513 (July 6, 1937).
[4] Minor, U. S. patent 2,157,243 (May 9, 1939).
[5] Willis and Felix, U. S. patent 1,045,234 (Nov. 26, 1912).
[6] Untiedt, U. S. patent 1,777,945 (Oct. 7, 1930).
[7] Snelling, U. S. patent 1,630,721 (May 21, 1927).
[8] Talalay, British patent 455,138 (Oct. 14, 1936).
[9] Marshall, U. S. patent 1,551,110 (Aug. 25, 1925); Denton, U. S. patent 1,905,269 (Apr. 25, 1933); Roberts, U. S. patent 2,086,513 (July 6, 1937); Pfleumer, U. S. patent 1,038,950 (Sept. 17, 1912).
[10] Beckmann, U. S. patent 1,745,657 (Feb. 4, 1930).
[11] Shriver and Jordan, *India Rubber World* **100**, 33 (1939).
[12] Fannenstiel, U. S. patent 1,142,619.
[13] Lindemann, U. S. patent 1,951,618 (Mar. 20, 1934).
[14] 1943 Supplement to Book of A.S.T.M. Standards, Part 3, p. 416.

STRAINS IN AN INFLATED RUBBER SHEET, AND THE MECHANISM OF BURSTING *

L. R. G. TRELOAR

Introduction.—In a study of the bursting of an inflated rubber sheet clamped round its circumference, Flint and Naunton[1] brought forward a number of interesting data both on the shape of the balloon formed and on the characteristic pattern of tearing. The balloon was shown to assume the form of a flattened spheroid. Formulas were given for the breaking strength and breaking elongation in terms of easily measurable parameters of the balloon in the fully distended state. More recently, the author has had occasion to make use of this type of inflation in the course of an investigation into the stress-strain relations for rubber in a two-dimensional extension, and it became necessary to explore the state of strain over the surface of the balloon, to see over what area the extension could be regarded as uniform. The results of this investigation are given in the first part of this paper; the second part reports some observations on the pattern of bursting of a variety of rubbers, and discusses the mechanism of bursting in the light of the stresses and strains in the sheet.

I. THE PRINCIPAL STRAINS IN AN INFLATED SHEET

Experimental arrangement.—The rubber used was a vulcanized latex sheet of thickness approximately 0.8 mm. (For formula of composition see No. 1, Appendix.) On a circular piece of 50 mm. diameter, seven concentric circles of radii approximately 2, 4, 6, ··· mm. were described. These, together with the central spot, gave fourteen intercepts on a specific diameter, which were measured by means of a traveling microscope to 0.01 mm. The sheet was then attached by means of a tight rubber binding, as in Figure 1, to the end of a

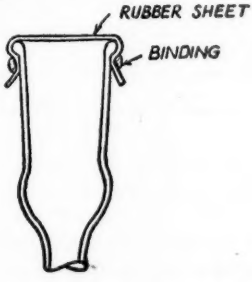

FIG. 1.—Mounting of rubber sheet for inflation.

conical glass tube having a slightly protruding rim. The external diameter of the rim was about 1 inch. To fold the sheet over the tube without forming kinks, it was necessary to apply a slight stretch to the rubber, corresponding to a radial extension of about 5 per cent.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 19, No. 6, pages 201–212, April 1944.

The tube was mounted vertically, and observations of the dimensions of the inflated balloon were made with a horizontally mounted microscope provided with horizontal and vertical travel. The specified diameter, which was initially at right angles to the line of sight, thus became the circumference of the vertical section of the inflated balloon, with the points such as A (Figure 2) corresponding to the intersections of the measured circles with the plane of section. The experiments consisted in measuring the horizontal and vertical position of each of these points round the circumference of the balloon. A typical plot of the points thus obtained is shown in Figure 2 (profile, 1).

In making the observations, the microscope cross-wire was focused on the center of the marked lines on the rubber, where these were visible. At the

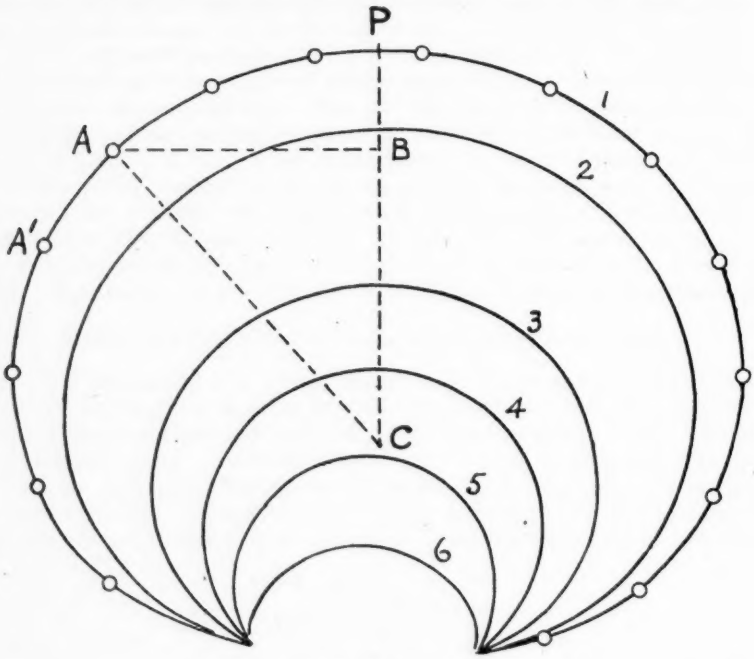

FIG. 2.—Longitudinal sections of inflated sheets.

highest distension some of the original lines were not visible in the microscope, though they were still visible to the unaided eye. In these cases the center of the line was given an additional marking with a pen.

Readings were taken at six different distensions. Two rubber sheets were used; the first gave the profiles 4, 3 and 2 (Figure 2) in that order, and the second the profiles 6, 5 and 1.

The principal elongations.—The measurements referred to above are sufficient to enable the state of strain at all portions of the sheet to be determined. Imagine a small circle of unit diameter drawn on the original sheet. On the inflated sheet this circle will, in general, appear as an ellipse, of which one axis, of length $(1 + e_v)$ will lie along a line of longitude through the pole P, and the other, of length $(1 + e_h)$, will lie along a line of latitude. The quantities e_v and e_h are called the principal elongations in the sheet, and will be referred to

as the longitudinal (or vertical) and latitudinal (or horizontal) elongations, or strains. From considerations of symmetry it follows that the horizontal strain is constant round a line of latitude, and that the two principal strains are equal at the pole.

The longitudinal strain.—The longitudinal strain was readily obtained from the observed data. If s is the length of the arc AA′ (Figure 2), and s_0 is the corresponding measured intercept on the undeformed sheet, then

$$e_v = s/s_0 - 1$$

is the mean vertical elongation over the interval AA′. This was taken to be the vertical elongation at a point midway between A and A′. The arc AA′ was obtained from the chord AA′, making use of the angle subtended by the

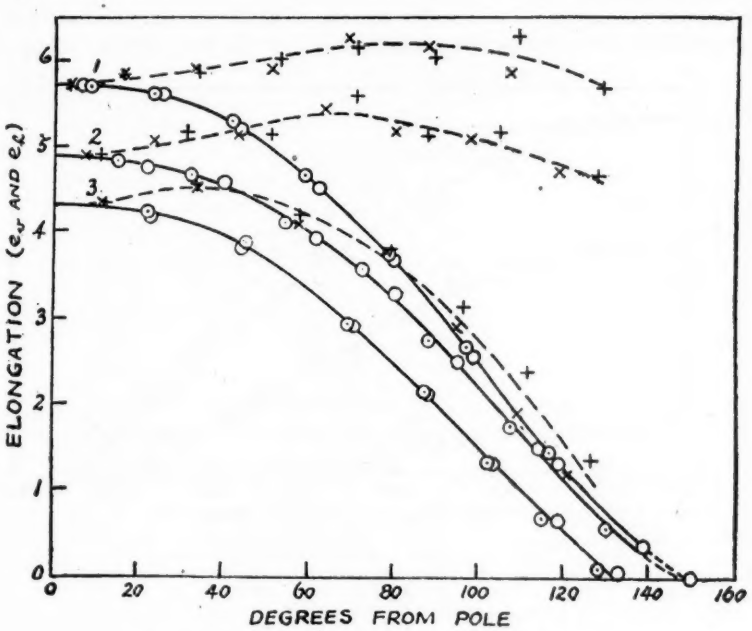

FIG. 3.—Principal elongations over surface of sheets 1, 2 and 3.
– – – – – longitudinal, e_v (× left, + right).
——— latitudinal e (⊙ left, ○ right).

arc AA′ at its center of curvature. The chord AA′ was calculated from the original microscope readings.

The latitudinal strain.—The point A lies on a circle of latitude of radius AB (Figure 2), where AB is perpendicular to the axis of symmetry PC. Thus if AB = r, and if r_0 is the distance AP on the unstretched sheet, the horizontal elongation e_h is $r/r_0 - 1$. The position of P on the unstretched sheet was deduced on the assumption of a constant longitudinal strain between the two marked points nearest to P. The value of r was found by measurement of the drawings of the profiles, or, for points close to P, by calculation from the geometry of the sphere.

Results.—The data obtained from the measurements of the six different distensions are presented in Figures 3 and 4, which show both the longitudinal

elongations (broken lines) and latitudinal elongations (solid lines), plotted against the latitude. This was represented, for convenience, as the angle from the pole, referred to the center of curvature C of the polar region as center. This is not the same as the center of the equatorial circle. Considering the state of strain at the highest distension, it is seen that at the pole $e_h = e_v$, and that on proceeding outwards from the pole e_h falls steadily to zero at the rim. On the other hand e_v first rises, then falls slightly, but remains large over the whole circumference. At the pole the strain corresponds to a simple compression (at right angles to the surface of the sheet), whereas at the edge the strain is a pure shear, as by definition, a shear is a deformation without change of volume, in which lengths parallel to a given direction remain unchanged ($e_h = 0$). At intermediate positions the strain may be regarded as intermediate between a compression and a shear.

The next distension, No. 2, shows a state of strain similar to that in No. 1. At lower distensions, there was a marked change in the relative values of e_v

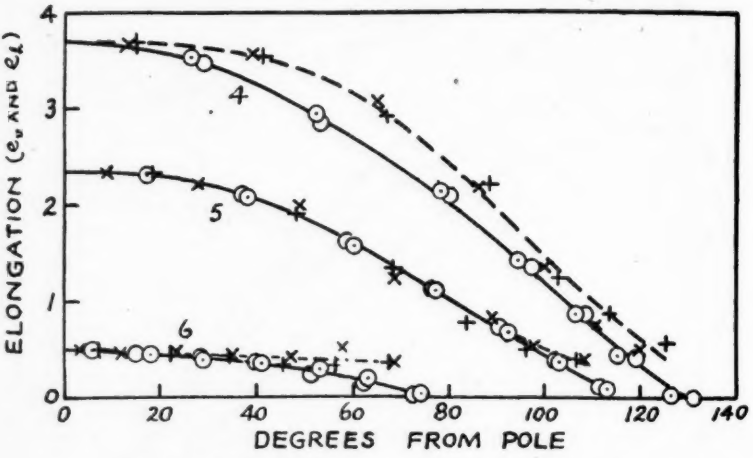

FIG. 4.—Principal elongations over surface of sheets 4, 5 and 6.
– – – – – longitudinal (× left, + right).
——— latitudinal (⊙ left, ○ right).

and e_h, the variations in e_h showing a progressive tendency to follow the variations in e_v. This was particularly marked in the case of No. 5, in which e_h and e_v were equal except in the immediate vicinity of the clamped edge. In this case the strain corresponded to a simple compression over nearly the whole of the surface, the amount of the compression diminishing from the pole outwards.

The thickness ratio.—From the two principal elongations it is possible, assuming that the volume is constant, to calculate the strain in the direction at right angles to the surface of the sheet. If α is the ratio of the thickness at any point to the thickness of the original sheet, then $1/\alpha = (1 + e_v)(1 + e_h)$. Table I gives the variation of α over the surface, for a typical high distension (No. 2) and a typical medium distension (No. 5).

Discussion of results.—Although the chief interest of the work lay in the practical question of determining the principal strains, there are certain interesting features of the data presented above which merit discussion.

TABLE I

VARIATION OF THICKNESS AND ORIENTATION OVER SURFACE OF BALLOON

Degrees from pole	Thickness ratio α		Ratio $\frac{1+e_v}{1+e_h}$
	No. 2	No. 5	No. 1
0	.0287	.0892	1.00
20	.0288	.0914	1.02
40	.0292	.105	1.10
60	.0312	.147	1.26
80	.0375	.250	1.53
100	.0514	.466	2.04
108	...	.603	...
120	.0815	...	3.07
127	.101	...	...
139	...	...	4.9

The complex variation of the principal strains with the degree of inflation is connected with the nature of the stress-strain relations for rubber under complex types of deformation. There are few data available which cover the more complex types of deformation; if there were, it might be possible to calculate both the form of the inflated sheet and the magnitude of the principal strains corresponding to a given value of gas pressure P. From theoretical considerations, it is possible to throw some light on the case of the intermediate distension (No. 5). It has been shown, on the basis of the kinetic theory of the elasticity of a molecular network[2], that, in a film stretched uniformly in two dimensions, the tension t across a line of unit length is related to the ratio α of the thickness in the stretched, to that in the unstretched state by the equation:

$$t = G(1 - \alpha^3) \tag{1}$$

where G is a constant. Hence for thicknesses less than about $\frac{1}{3}$, corresponding to principal elongations exceeding 70 per cent, the tension in the sheet is substantially independent of extension.

In general, the surface of a sheet under tension is characterized by two principal radii of curvature, r_1 and r_2, corresponding to the two principal extensions. If t_1 and t_2 are the respective tensions per cm. in these directions, it can be shown that the equilibrium fluid pressure P is given by the formula:

$$P = t_1/r_1 + t_2/r_2 \tag{2}$$

If the sheet is everywhere in a state of simple compression, then $t_1 = t_2$, and if also it is spherical, Equation (2) reduces to the well-known form $P = 2t/r$, so t, the tension, must be constant over the surface. That t may be constant even though the compression varies is to be expected from Equation (1). Thus it is readily understood that the sheet for which the two principal extensions are everywhere nearly equal (No. 5) is the one which approximates most nearly to the spherical form. Indeed, this experimental fact provides a rather neat demonstration of the validity of Equation (1).

Another interesting feature of the data is the increase of e_v on proceeding outwards from the pole, in the case of the highest distensions. In this high state of strain the molecular network is extended to the point where many of the molecules are stretched out nearly to their fullest extent, and the simple molecular network theory with the resulting equation (1) no longer applies. Examination of the profiles for the high distensions shows a close approximation to sphericity to an angle of about 60° from the pole. From purely geometrical

considerations, if a sheet is distorted into a sphere, one of two effects must occur. Either the thickness varies over the surface, in which case the two principal strains may remain equal (as in No. 5, discussed above), or the thickness remains constant, but the principal strains are unequal. Table I shows that in a typical high distension (No. 2) the thickness remains approximately constant over the spherical region (0 to 60°), although the separate extensions (Figure 3) vary considerably.

Referring to Equation (2), in the spherical region $r_1 = r_2$, and therefore $t_1 + t_2 =$ constant. Thus, as the distance from the pole increases, the longitudinal tension increases, and the latitudinal tension is reduced in such a way that their sum remains constant and equal to its value at the pole. The assumption made by Flint and Naunton (*loc. cit.*) that the longitudinal tension is constant over the surface, is thus seen to be unjustifiable.

II. THE MECHANISM OF BURSTING

Introduction.—Flint and Naunton[1] made the interesting discovery that, in the process of bursting, an inflated sheet develops a number of radial tears starting at the center and terminating on a well-defined circle, the appearance resembling that of the petals of a flower. They pointed out that undercured rubbers give none, the entire center portion of the sheet being removed on bursting. The suggestion was made that the radial type of burst was due to a sort of cleavage resulting from an orientation of the molecules along the lines of longitude of the inflated sheet.

In this section this suggested explanation is examined in the light of the more exact knowledge of the strains in the inflated sheet now available. An alternative explanation is put forward which seems to be in better accord with the facts. Before these theories are discussed, some further observations of the types of burst for a variety of different rubbers will be presented.

Bursting tests on various rubbers.—For the bursting of sheets the simple device shown in Figure 1 was not satisfactory, and a firmer type of clamp had to be used. Details of this clamp are shown in Figure 5. The rubber was

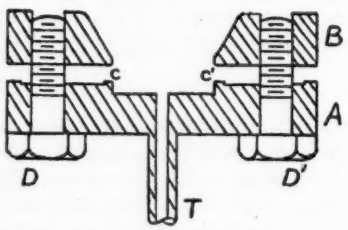

FIG. 5.—Section of circular clamp used for bursting tests.

gripped between the circular raised projection *cc'* on the bottom plate A and the plane surface of the top plate B, the latter containing a circular aperture of 1 inch diameter opening outwards in the form of a cone of semivertical angle 30°. Pressure was applied by means of 4 bolts DD'. The sheets were inflated through the tube T by means of a bicycle pump.

The samples tested included a vulcanized latex sheet, a normally milled, and an exceptionally lightly milled smoked sheet vulcanizate without fillers, a smoked sheet tire-tread vulcanizate, a GR-S (butadiene-styrene) synthetic

rubber mix containing 50 per cent clay, and a GR-S tire-tread mix. Details of the compounding of these samples are given in the Appendix. The latex sheet (No. 1) was the same as that used in the measurement of the strains described in Part I. The tests were made at room temperature (20–22° C). The time taken to burst was of the order of 10 seconds. In most cases some of the petals were blown off; these were collected in a loosely-fitting cloth bag surrounding the balloon and subsequently counted. The tensile properties of the sheets were measured by means of a Goodbrand tensile-testing machine. From the tensile data the actual Young's modulus at break was calculated from the dimensions of the strip at the breaking point. The measured slope of the stress-strain curve is $Y = \frac{\Delta F/A_0}{\Delta l/l_0}$ where ΔF is the increase in force, referred to the original section A_0, corresponding to an increase in length Δl, and l_0, is the original length. The actual Young's modulus is $Y^1 = \frac{\Delta F/A}{\Delta l/l}$, where l and A are the actual length and sectional area at break. But $l_0A_0 = lA$, hence $Y^1 = Y.(l/l_0)^2$. This formula enables the actual modulus to be calculated from the stress-strain curve. The following table shows the total number of petals formed, the number remaining attached to the sheet, and the Young's modulus at break, for each of the rubbers examined.

Observations on data.—The first point to be observed is that the petal type of burst is general; indeed, the normal type of burst in rubber sheet, for, with one exception, all the rubbers listed in Table II showed the phenomenon.

TABLE II

SUMMARY OF BURSTING-TEST DATA

Rubber	Number of petals			Actual Young's modulus at break (kg. per sq. cm.)
	Total	Attached	Mean total	
1. Latex	45	39	33	16,400
	34	24		
	19	14		
2. Smoked sheet normal milling 10 min. vulcanization	14	9	12.4	10,500
	11	2		
3. Smoked sheet normal milling 30 min. vulcanization	11	4	10	5,500
	9	6		
4. Smoked sheet light milling	15	2	10	7,900
	8	2		
	6	0		
5. Smoked sheet tire tread	23	7	16	3,020
	18	8		
	15	11		
	7	4		
6. GR-S clay	...	...	No petals formed	162
7. GR-S tire tread	8	2	7.3	3,730
	7	2		
	7	3		

There were differences in the perfection of the burst, not only between different rubbers, but also between different samples taken from the same sheet. This latter effect makes a detailed comparison of different rubbers rather difficult. Certain outstanding effects are, however, to be observed:

The total number of petals, as well as the proportion remaining attached, was highest for the latex rubber. This rubber gave also the highest tensile

strength (310 kg. per sq. cm., referred to original dimensions), and Young's modulus at break (16,400 kg. per sq. cm., referred to actual dimensions).

The only rubber which gave no evidence of petal-formation was the GR-S clay mixture, which also had the lowest tensile strength (24 kg. per sq. cm.) and Young's modulus at break (162 kg. per sq. cm.).

The GR-S tire tread gave evidence of rather fewer petals than the smoked sheet tire tread. Otherwise the appearance was the same for both rubbers. This shows that crystallization has no important bearing on the phenomenon, since GR-S does not crystallize under any conditions.

Photographs of typical bursts are given in Figure 6.

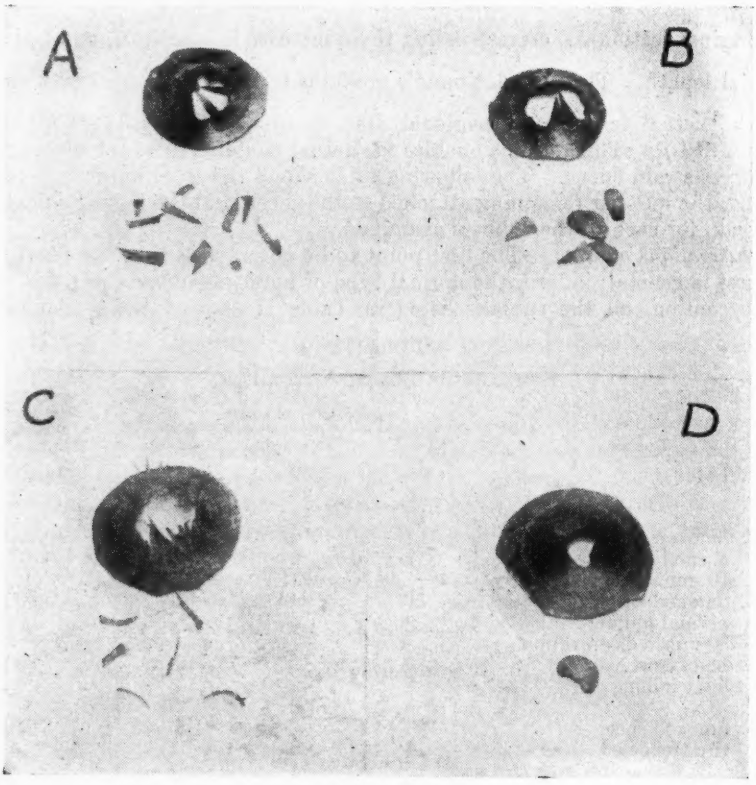

FIG. 6.—Sample bursts.
A. Smoked sheet rubber tire tread (No. 5).
B. GR-S tire tread (No. 7).
C. Latex rubber (No. 1).
D. GR-S-clay (No. 6).

The mechanism of bursting.—In the theory advanced by Flint and Naunton[1] in explanation of the radial pattern of tearing, the basic concept is that of a radial orientation of the molecules of the sheet, with the pole as center. It is pointed out that the pole is the thinnest, and therefore the weakest point. The original point of bursting is, therefore, at the pole. This initial rupture is, it is suggested, followed by a cleavage, or tearing of the molecules parallel to their main direction, *i.e.*, radially.

The knowledge now available enables this hypothesis to be examined in a more quantitative manner. From the two principal extensions it is possible to obtain a figure which is closely related to the degree of orientation at each point of the sheet. This is the ratio $(1 + e_v)/(1 + e_h)$ of the principal axes of the strain ellipsoid. Table I gives the numerical values of this ratio for the most highly distended sheet (No. 1). A ratio of 1.0 represents no orientation. In the central region, that is, up to 60° from the pole, the orientation is slight. This probably covers the area in which the general pattern of bursting is generated. Even at 100° from the pole, the ratio $(1 + e_v)/(1 + e_h)$ is only 2.0. By comparison, a high degree of orientation, corresponding to a simple elongation of 700 per cent, would be represented by $(1 + e_v)/(1 + e_h) = 22.6$. It is to be concluded that the molecular orientation over the region of bursting is nowhere high enough to give a marked anisotropy of mechanical properties, such as exists, for example, in a highly extended strip.

Furthermore, even this moderate degree of radial orientation probably disappears as soon as the bursting commences, as will be seen from the following discussion.

Alternative theory of bursting.—Suppose a small hole appears in the neighborhood of the pole, as in Figure 7. The radial, or longitudinal, tension t_1 must

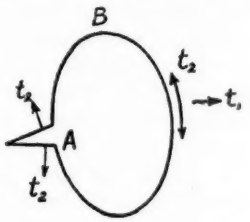

FIG. 7

fall to zero at the edge of the hole, and the rubber in the immediate vicinity of the hole will be in a state of strain under the influence of the single circumferential, or latitudinal tension t_2, as in a simple elongation. Thus when a hole is formed, the molecular orientation will change from radial to circumferential. As the size of the hole increases (under the influence of the tension t_1) the length of the circumference, and therefore also the tension t_2 increase, until the ultimate strength is reached, when failure occurs by cracking or tearing at right angles to the tension t_2. This mechanism therefore explains in a general way the existence of radial cracks.

The remaining question to be considered is why a large number of tears occur apparently simultaneously. To understand this, suppose that the first crack starts at A, and travels radially outwards with a high velocity. As the crack opens, the effect of the relaxation of the stress t_2 spreads out sideways with a finite velocity, and does not reach another point B until a definite time interval has elapsed. Meantime, the stress t_2 at B is still increasing as the hole expands, and another crack may start at B and run out independently of anything that may be happening at A. Thus a large number of radial cracks may run out apparently, though not necessarily exactly, simultaneously. On this view, there will be a certain minimum distance between cracks, determined mainly by the relative rates of transmission of the crack and of the elastic relaxation process. This theory accounts for the existence of radial cracks, as well as for their regular spacing.

The explanation advanced to explain the radial cracking suggests a rather close similarity between this type of fracture and the fracture of a sheet of glass by impact. Though it is not suggested that the two processes are identical, it does seem probable that the characteristic radial cracking is due in both cases to the same fundamental causes, that is, to a velocity of crack propagation so high that in the time taken for a crack to run, the strain is relieved only over a small area. In a typical glass the crack velocity is about 1500 meters per second[3]. Generally, brittle fracture of the glassy type is associated with a small capacity for storing or dissipating energy, and occurs in materials having a high modulus of elasticity and small extensibility. The radial cracking in a highly stretched rubber would, therefore, appear to be a consequence of its high effective modulus of elasticity in this state, and a correlation might be expected between the Young's modulus at the moment of bursting and the number of radial cracks. The Young's moduli at break, calculated from tensile tests, for the rubbers whose bursting was examined, are given in Table II. These figures do not necessarily give a correct measure of the effective modulus in the inflated sheet, first because the breaking strength and modulus in a two-dimensional extension are not necessarily the same as in a one-dimensional extension, owing to the differences in molecular orientation, crystallization, etc. in the two cases, and second, because the data from a slow tensile test are affected by molecular relaxation, and therefore indicate a lower modulus than that which would be effective in a rapid process. However, they give some indication of the order of magnitude of the modulus at break, and probably place the different rubbers in the correct order. From Table II it is seen that the moduli range from 162 kg. per sq. cm. in a rubber giving no petals to 16,400 kg. per sq. cm. in the rubber giving the most perfect petal formation. The remaining rubbers are intermediate both in moduli and number of petals formed, but a definite correlation between the two properties cannot be traced.

For small elongations the latex rubber (No. 1) had a Young's modulus of about 10 kg. per sq. cm. The final figure of 16,400 kg. per sq. cm., represents an increase by a factor of more than 1600. For comparison, the Young's modulus of glass is about 600,000 kg. per sq. cm. The stretched rubbers are thus intermediate in hardness, and, on a logarithmic scale, have mechanical properties rather closer to those of a glass than to those of a rubber in the normal state.

SUMMARY

The two principal strains in a circular sheet of rubber clamped round its circumference and inflated are measured at all points on the surface of the spheroidal balloon thus formed. The principal strains may show relatively large variations over an area in which the form is nearly spherical and the thickness is approximately constant. The reasons for this, and for certain other effects brought out in the experiments, are discussed.

In experiments on the bursting of sheets of various rubbers (natural and synthetic), there appeared to be a general relation between the hardness at the instant of breaking and the number and regularity of the radial tears. From the strain measurements it is concluded that these radial tears are not caused by the relatively slight radial orientation of the molecules in the sheet. A detailed mechanism of bursting is suggested, in which the radial tears are compared with the radial cracks associated with glass fractures.

ACKNOWLEDGMENT

The author desires to express his thanks to E. Rhodes, who was responsible for the preparation of the samples and for the tensile tests. The work forms part of the program of fundamental research on rubber undertaken by the Board of The British Rubber Producers' Research Association.

APPENDIX. COMPOUNDING FORMULAS

No. 1

Latex rubber	100
Sulfur	1.5
Zinc oxide	1
Sodium diethyldithiocarbamate	0.5

Vulcanized 30 minutes at 100° C

No. 2

Smoked sheet rubber	100
Sulfur	3
Zinc oxide	5
Stearic acid	1
Mercaptabenzothiazole	0.5

Vulcanized 10 minutes at 142° C

No. 3

Ditto

Vulcanized 30 minutes at 142° C

No. 4

Smoked sheet rubber milled to Mooney value of 71 at 100° C	100
Sulfur	1.5
Zinc oxide	1
Zinc diethyldithiocarbamate	0.5
Stearic acid	0.5

Vulcanized 1 hour at 100° C

No. 5

Smoked sheet	100
Benzothiazyl disulfide	1
Zinc oxide	5
Stearic acid	2
Carbon black	50
Pine tar	3
Nonox-S	1.5
Sulfur	3

Vulcanized 45 minutes at 142° C

	No. 6	No. 7
GR-S	100	100
Benzothiazyl disulfide	1	1
Diphenylguanidine	0.25	0.25
Zinc oxide	5	5
Stearic acid	1	1
China clay	50	...
Carbon black	...	50
Pine tar	3	3
Sulfur	2	2

Vulcanized 45 minutes at 142° C

REFERENCES

[1] Flint and Naunton, *Trans. Inst. Rubber Ind.* 12, 367 (1937).
[2] Treloar, *Trans. Inst. Rubber Ind.* 18, 256 (1943).
[3] Preston, *J. Applied Physics* 13, 623 (1942).

IDENTIFICATION OF NATURAL AND SYNTHETIC RUBBERS *

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The use of synthetic elastomers as substitutes for natural rubber has given rise to a need for a rapid method by which these materials can be distinguished from one another. The methods of identification available can be divided into two groups: those which depend on the personal judgment of the operator, such as physical appearance and the odor produced on combustion, and those which depend on detailed chemical tests. A method is proposed which is believed to be more reliable than the former, and does not require the detailed laboratory manipulations necessary for a complete analysis. The method was designed for the identification of soft-rubber vulcanizates based on the polymer types represented by natural rubber, Buna-S, Buna-N, Butyl, Neoprene-GN, chloroprene-nitrile polymers, polyvinyl chloride, and polyvinyl acetate. Distinctions within types are not possible. The polysulfide rubbers are not included, as they can usually be recognized by odor.

Identifications made on the basis of physical appearance and flame tests are discussed by Kluckow[1] and Nechamkin[2]. Mark and Raff[3] describe the application of some simple chemical tests, such as those for nitrogen, chlorine, and sulfur. The chromic acid oxidation of natural rubber to acetic acid is described by Kuhn and L'Orsa[4]; Burger, Donaldson, and Baty[5] describe a quantitative procedure based on this reaction. A method for the detection of natural rubber, which depends on the development of a purple color when the brominated product is reacted with phenol, was given by Weber[6] and was further developed by Kirchhoff[7]. The method was modified by Romeyn[8] and applied to the testing of synthetic rubbers. Experiments conducted in this laboratory indicate that Buna-N can be detected by the hydrolysis of the nitrile group to an ammonium salt in the presence of sulfuric acid. The relative resistance of the hydrocarbon rubbers to the action of strong oxidizing agents has also been investigated, but the results tend to vary widely with the type of compounding.

Reliable results have been obtained by the use of a procedure which depends on an approximate determination of the pH and specific gravity of the pyrolysis products. The tests are simple to apply, and can readily be combined into a single test capable of distinguishing six of the eight types considered.

A sample of the polymer is dry-distilled under standardized conditions and a portion of the distillate is collected beneath the surface of two previously prepared solutions. Solution I is yellow, and is buffered at a pH of 4.7 with a citric acid–sodium citrate mixture. It contains thymol blue and bromothymol blue, and the specific gravity is adjusted to 0.850 with methyl alcohol. Solu-

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tion II is blue, and contains sodium citrate and bromophenol blue. The pH is adjusted to 8.4 and the specific gravity to 0.890.

The color changes which the solutions undergo at different pH values are indicated in Figure 1. The cross-hatched areas show the transition intervals. Table I describes the changes which take place in the two solutions when the

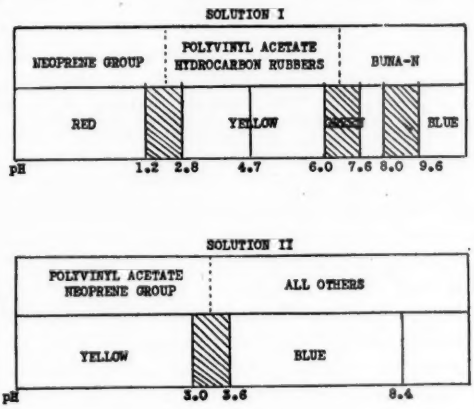

FIG. 1

pyrolysis products from the substances considered are distilled into them. Buna-N and other similar materials yield ammonia and amines in sufficient quantity to produce a green color in solution I. If solution I becomes red and solution II yellow, the presence of a compound containing chlorine, such as Neoprene-GN, chloroprene-nitrile polymers, or polyvinyl chloride, is indicated. Polyvinyl acetate produces acetic acid and both solutions become yellow.

Natural rubber, Buna-S, and Butyl yield neutral products which do not materially affect the color of either solution. They are distinguished from one

TABLE I

PYROLYSIS PRODUCTS

Group	Rubber Type	Color of Solution		Density Behavior of Condensate	
		I	II	I	II
Blank	...	Yellow	Blue	...	...
(1)	Buna-N	Green	Blue	Sinks	Sinks
(2)	Neoprene-GN Chloroprene-nitrile Polymers Polyvinyl chloride	Red	Yellow	Sinks	Sinks
(3)	Polyvinyl acetate	Yellow	Yellow	Sinks	Sinks
(4)	Buna-S	Yellow	Blue	Sinks	Sinks
(5)	Natural rubber	Yellow	Blue	Sinks	Floats
(6)	Butyl	Yellow	Blue	Floats	Floats

another by differences in the specific gravities of their pyrolysis products as indicated by their behavior in the two solutions (Table I). Table II shows some typical values for the decomposition products of the three materials.

In the case of natural rubber it is known that volatile hydrocarbons are formed which do not condense under the conditions of the test[9]; the values

TABLE II

SPECIFIC GRAVITIES AT 25°/4° C

	Gum Rubber	Cured
Butyl	0.843	0.842
Natural rubber	0.860	0.873
Buna-S	0.935	0.925

obtained, therefore, depend on a successful reproduction of the experimental conditions. The oil produced from Buna-S sinks to the bottom of the test-tubes in both solutions, while that from natural rubber sinks in solution I but floats in solution II. Butyl rubber produces a white, difficulty condensable vapor and a small amount of a straw-yellow oil, which floats on the surface of both solutions.

Several additional tests are necessary for confirmatory purposes and to distinguish between substances which fall in the same group. Buna-N on pyrolysis produces small quantities of cyanides, which are detected by the familiar Prussian blue test. This reaction is also of value in establishing the presence of nitrile nitrogen in chloroprene-nitrile mixtures. The Beilstein test is of value for the detection of polymers containing chlorine, particularly when other polymers are present. Neoprene-GN is distinguished from polyvinyl chloride by the fact that compounds based on it rapidly decolorize a solution of iodine in carbon tetrachloride. The Weber test[6] for natural rubber is of value for confirmatory purposes and for the detection of mixtures. The test may be applied directly to compounded samples without previous treatment.

The rubber is brominated and heated with phenol, and the melt is diluted with chloroform. Natural rubber produces an opaque purple solution, Buna-S a colorless to a faint purple solution, Neoprene a brown solution, and Buna-N a colorless solution[8]. These colors may be modified by the presence of soluble compounding ingredients, but the color produced from natural rubber is always recognizable. A colored flow chart showing the reactions obtained is useful for the interpretation of results and the instruction of plant operators.

APPARATUS

When only a few tests are to be made, the use of 16 × 150 mm. Pyrex test-tubes equipped with glass condensing arms is satisfactory. A Bunsen burner adjusted to give a blue cone is a convenient source of heat.

For large-scale testing, an electrically heated furnace of the type shown in Figure 2 is desirable. The well contains a metal casting bored to accommodate three 16 × 100 mm. quartz tubes. The depth is adjusted so that 4 cm. of the length of the tubes project. The temperature of the metal block is regulated by a rheostat at 530° to 550° C. Side arms made from Pyrex tubing, 5 mm. in outside diameter, having a horizontal length of 12 cm. and a vertical length of 6 cm., are provided. After completing a test, the residue is removed from the quartz tube by ignition and the side arm cleaned with carbon tetrachloride.

REAGENTS

Solutions I and II are prepared according to the formulas and the specific gravities determined. They are adjusted with methyl alcohol or water to within ±0.0005 of the required value. Two-cc. portions are placed in 10 × 75-mm. test-tubes, and kept tightly stoppered before use.

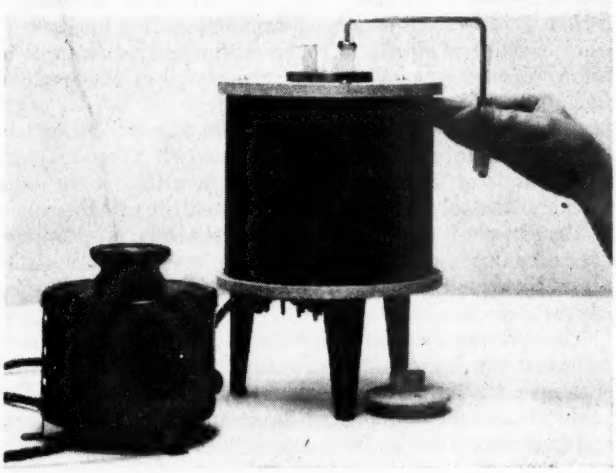

FIG. 2

Solution I contains 0.5 gram of sodium citrate ($2Na_3C_6H_5O_7.11H_2O$), 1.00 gram of citric acid, 0.04 gram of thymol blue, and 0.10 gram of bromothymol blue dissolved in a mixture of 1000 cc. of methyl alcohol and 210 cc. of water. The pH is 4.7 at 25° C, and the specific gravity 0.850 at 25°/4° C.

Solution II contains 2.00 grams of sodium citrate and 0.01 gram of bromophenol blue dissolved in a mixture of 780 cc. of methyl alcohol and 380 cc. of water. The pH is 8.4 at 25° C, and the specific gravity 0.8900 at 25°/4° C.

The following reagents are required for carrying out the confirmatory tests: 5% ferrous sulfate solution containing 1 cc. of concentrated hydrochloric acid per 100 cc., 5% sodium hydroxide solution, 10% hydrochloric acid solution, 55% sulfuric acid solution (by weight), a solution of iodine in carbon tetrachloride containing 0.2 gram per liter, bromine, and phenol.

GENERAL PROCEDURE

The rubber is stripped from adhering fabric, and a 1-gram sample placed in a quartz tube. A side arm is attached and the tube placed in the furnace at 530° to 550° C. After about 1 minute the sample begins to decompose. When droplets of condensate appear in the vertical section of the side arm, the end is dipped beneath the surface of 2 cc. of solution I contained in a 10 × 75-mm. test-tube. After 5 to 10 seconds, or when enough oil has collected to cover the surface of the liquid, the tube is removed and the process repeated with solution II. The tubes are cooled for a few minutes until thermal equilibrium is established and then shaken sharply to determine whether the droplets formed will sink or float. The colors of the solutions and the positions of the droplets are noted and the sample is classified according to the information provided in Table I.

CONFIRMATORY TESTS

Group I.—The presence of Buna-N is confirmed by combining the contents of the tubes used in the initial test and adding 1 drop of sodium hydroxide

solution, and 1 cc. of ferrous sulfate solution. The tube is heated gently for a minute and then acidified with hydrochloric acid. If a fine green precipitate is formed, the presence of nitrile nitrogen in the original sample is indicated. The suspension appears green under the conditions of the test, owing to the presence of the indicators.

Group II.—The Prussian-blue test described above distinguishes between Neoprene-GN and chloroprene-nitrile polymers.

A 0.2-gram sample of the elastomer is shaken with 2 cc. of iodine solution. If the violet color noticeably fades in 2 to 3 minutes, the sample is Neoprene-GN; if it persists, the sample is based on polyvinyl chloride.

Group III.—A 0.2-gram sample is placed in a test-tube with 2 cc. of 55% sulfuric acid, and warmed gently. If decomposition occurs, the compound is based on polyvinyl acetate.

Group IV–V.—To detect possible interference from the presence of asphaltic extenders in the test which distinguishes natural rubber from Buna-S, a 0.2-gram sample is shaken with 2 to 3 cc. of chloroform. If the chloroform darkens noticeably, the test should be repeated on a sample which has been extracted for 4 hours with chloroform[10] and dried in a vacuum oven for 1 hour at 70° C or equivalent.

To provide a further distinction between natural rubber and Buna-S, the Weber test is of value. A 0.1-gram sample is placed in a test-tube, and a drop of bromine is added. The tube is heated gently without charring the contents, and the excess bromine is removed in a current of air. The sample is then covered with phenol and heated gently for a few minutes. After cooling, 10 cc. of chloroform is added. An opaque purple solution is formed if natural rubber is present. Extracted samples of Buna-S give pale violet to colorless solutions, but compounded samples give solutions ranging from a light yellow to a deep brown. It has been reported that as little as 10 mg. of rubber can be detected by this reaction[8].

Group VI.—The destructive distillation of Butyl rubber yields a white, difficulty condensable vapor. A light-yellow mobile oil is obtained.

DISCUSSION

The tests described have been applied to various materials, including tires, tubes, mechanical goods, oil-resistant tubing, and gas-tank linings. They have been successfully used to identify reclaims made from natural rubber, Buna-S, Buna-N, and Neoprene-GN. For routine factory testing, the initial pyrolysis procedure supplemented by the Prussian-blue test is adequate. The auxiliary tests described are of value when a referee method is desired.

A complete discussion of the limitations and interferences would be too extensive for review, but a few specific examples are of interest. Although the presence of citric acid and sodium citrate in the test solutions ordinarily supplies sufficient buffering action to prevent interference from minor amounts of compounding ingredients, the presence of large amounts of fabric in a sample may influence the result. In the case of Buna-N, for instance, the initial green color reaction is not produced, and the sample may be confused with Buna-S. This difficulty can be overcome by first removing the fabric or by applying the specific Prussian-blue test. Buna-S samples compounded with 5 parts of a diaryl amine antioxidant were not sufficiently alkaline on pyrolysis to produce a color change. Similar compounds accelerated with 0.75 part of hexamethylene tetramine were also tested successfully.

An investigation of the reliability of the tests, based on the differences in the specific gravities of the pyrolysis products, indicates that, although compounds can be made up in the laboratory which do not fall within the scope of the method, they are not representative of the great majority of compounds which are encountered in actual practice. An increase in the combined sulfur content tends to increase the specific gravity of the pyrolysis product obtained from natural rubber. However, samples containing 5 parts of combined sulfur can be tested successfully. Low-melting asphaltic softeners do not interfere in amounts up to 10 parts. Mineral rubber does not interfere, as the rubber decomposition products distill over first. In making tests on compounds of this type, it is necessary to control pyrolysis temperature carefully, and follow the details of the procedure. The first portion of the distillate which comes over should be tested rather than that portion which is obtained on prolonged combustion. Interferences from extenders in amounts greater than those stated can be eliminated by a preliminary chloroform extraction, or the test can be confirmed by the use of the Weber color reaction.

The detection of mixtures has not been discussed. While many identifications can be made by the methods described, in some cases the analytical techniques involved are not readily adaptable to factory procedure.

SUMMARY

A method is described for identification of the types of elastomers most frequently encountered in the rubber industry. The initial test depends on qualitative measurement of the pH and specific gravity of the pyrolysis products. It can be carried out in a field laboratory in 3 to 4 minutes and will provide sufficient information for a classification of the sample.

REFERENCES

[1] Kluckow, *Chem.-Ztg.* **65**, 109 (1941).
[2] Nechamkin, *Ind. Eng. Chem. Anal. Ed.* **15**, 40 (1943).
[3] Mark and Raff, "High Polymers", Interscience Publishers, New York, 1941, Vol. 3, p. 37.
[4] Kuhn and L'Orsa, *Z. angew. Chem.* **44**, 847 (1931).
[5] Burger, Donaldson and Baty, ASTM Bulletin No. **120**, Jan. 1943, p. 23; RUBBER CHEM. TECH. **16**, 660 (1943).
[6] Weber, *Ber.* **33**, 791 (1900).
[7] Kirchhoff, *Kautschuk* **4**, 190 (1928).
[8] Romeyn, unpublished work, General Laboratories, U. S. Rubber Co., Passaic, N. J.
[9] Midgley and Henne, *J. Am. Chem. Soc.* **51**, 1216 (1929); RUBBER CHEM. TECH. **2**, 441 (1929).
[10] Am. Soc. Testing Materials Standards 1941 Supplement, Chemical Analysis of Rubber Products, D297–41T, p. 466.

PHYSICAL TESTING OF SYNTHETIC-RUBBER PRODUCTS *

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Evaluation that will predict with a high degree of accuracy the suitability for service of any product is the object of all physical testing. Over a comparatively short period of about twenty-five years, rubber technologists have evolved a series of tests which have evaluated natural rubber compounds reasonably well. When it became necessary to evaluate rubber substitutes, it was only natural that the same tests would be applied. The results obtained convinced everyone that these materials were definitely not equivalent substitutes, and to use them involved more than just replacement. Although the background is not so extensive as might be desired, the A.S.T.M. Committee D-11 on Rubber Products has learned enough about these materials to be able to present certain facts and recommendations to industry in general with regard to specifications covering synthetic rubbers and products made from them.

The entire field of physical testing is quite extensive, as it covers not only finished products but the component raw materials from the time they are received until they emerge as final products ready to be put into service. Also, in this large field, not everyone is interested in the same phase of testing synthetic rubber products. Tire development engineers are not interested in load deflection figures, which are so essential to automobile design engineers, and the latter have no concern with adhesion to fabric which must be considered by the pneumatic tire technologists and those concerned with hose and belting. This paper is intended to deal primarily with some of the physical properties which affect the service of finished products.

The major synthetic rubbers vary greatly in composition and physical properties. However, we can treat the entire group as a whole, and the exceptions will not be so large in number as to be confusing. Compared to the physical properties of natural-rubber compounds, the characteristics of synthetic-rubber compositions are much more affected by any change in the service or testing temperature. Definitely, the test engineer must evaluate at higher or lower than normal testing temperatures depending on those which the product under test may encounter in service. Before Pearl Harbor, rubber technologists had done some work along the lines of testing at elevated temperatures. However, with the introduction of synthetic rubbers it became mandatory that testing be done under these conditions because the synthetic materials have a definite tendency to generate more heat in service than the natural products. In addition, the high-flying airplane, which uses a considerable amount of rubber, has made it necessary to know the behavior at very low temperatures. Today, making physical tests at normal temperature is only part of the true evaluation.

* This is one of thirteen papers comprising a "Symposium on the applications of synthetic rubbers" at the 1944 Spring Meeting of the American Society for Testing Materials, held at Cincinnati, Ohio, March 2, 1944. It is reprinted here from the Society's booklet containing the complete symposium.

In preparing specifications for natural rubber products, the first two properties covered were hardness and tensile strength; in fact, placing the proper limits on these two properties in many cases definitely established the quality and type of compound desired. This is not the case with synthetic rubber, because ultimate tensile strength is not a satisfactory criterion of its quality. Ultimate tensile strength never bore too close a relation to service performance even with natural rubber, but we were able to use this value as a measure for quality classification. Indications with synthetic rubbers are that judgment of probable performance based on ultimate tensile strength may be even more misleading, because we know definitely that synthetic-rubber tire treads with half the tensile strength of the natural rubber controls have given comparable or even better service on the road. The tensile strength of a natural-rubber tread stock containing no reclaimed rubber usually was in excess of 4000 psi. The ultimate tensile strength of the synthetic-rubber passenger tire treads that are now being evaluated is seldom more than 2600 lbs. per sq. in., and for some that have given good service it is as low as 1900 lbs. per sq. in. Today the

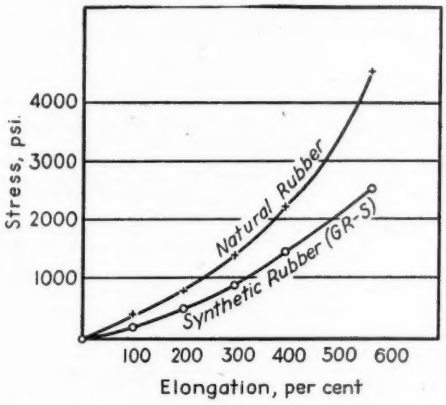

FIG. 1.—Typical stress-strain curves of tread stocks (A.S.T.M. Method D 412–41).

experienced technologist uses ultimate tensile strength values only as an evidence of how well the pigment has been dispersed. In other words, tensile strength can be used as a quality control of the same stock, but cannot be used to compare that stock with any other. Representative stress-strain curves of natural-rubber and GR-S tread stocks are shown in Figure 1.

The reliable determination of hardness values with current testing instruments is subject to difficulty. Hardness determinations by indentation methods are subject to personal error resulting from variations in pressure and time of reading, as well as to instrument variables. The only hardness determinations that can be relied upon at all for rubber are those similar to the A.S.T.M. Standard Method of Test for Hardness of Rubber[1], where definite pressures are exerted on the foot and point, and a definite time between application and reading is specified. This is important and essential because of the tendency of many synthetic rubber compositions to yield under load, due to their different elasticity characteristics. A recent paper by Taylor[2] discussed this tendency, and gave data that were obtained when the personal error had been eliminated. One of the charts presented in this paper is shown in Figure 2.

The standard A.S.T.M. reading time is 30 seconds after application of the load, and from the chart one can realize that some stocks at this period are still flowing quite rapidly.

The tensile stress determination and the measurement of elongation at break can be obtained on the same test-specimen while an ultimate tensile strength determination is being made[3], and these first two properties are of more value than the latter in judging the quality of synthetic-rubber stocks.

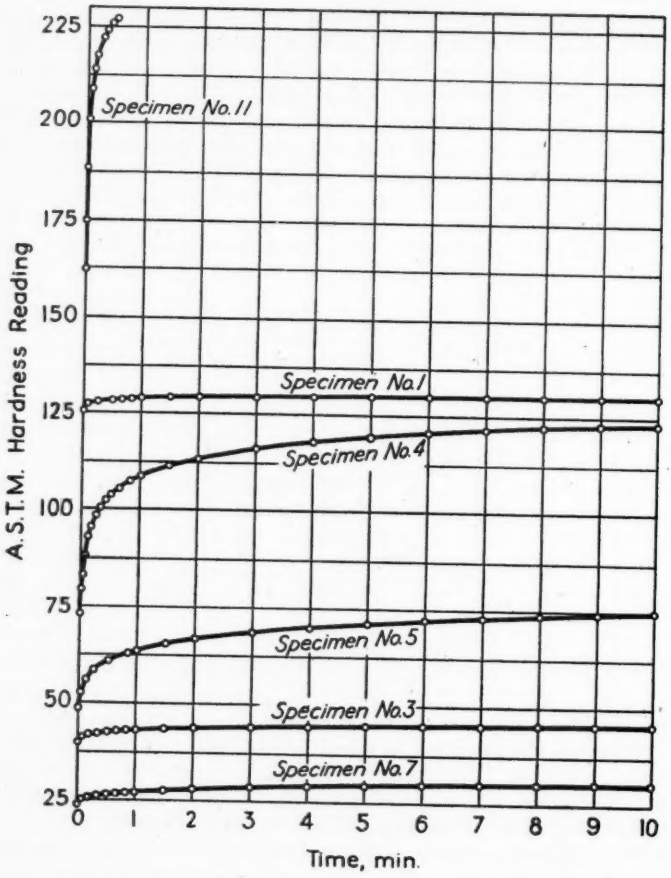

FIG. 2.—The relation of readings of A.S.T.M. hardness tester to time.

The vulcanization of various synthetic rubbers differs considerably from the chemical reaction which occurs when curing natural rubber, and therefore it is only natural that the change in physical state should not be the same as with natural rubber. The tensile stress value can be used to determine the stiffness or rigidity of the cured stock, and a comparison of the tensile stress figures, obtained on various cures of the same compound, gives a good idea of the rate at which vulcanization is taking place and of the time when further marked change in this physical property no longer takes place. At this time of cure,

it is usually felt that vulcanization has reached a maximum point. The value for the percentage of elongation at break also gives some idea as to rigidity, but its main use is to show the tendency to become brittle. In Figure 3, a comparison is shown of tensile stress determinations over a range of cures.

The tensile stress and ultimate tensile strength determinations on vulcanized synthetic rubbers are being made on the standard rubber tension test machines. The rate of applying the load has not been changed from the original 20 inches per minute which was used for rubber, but every test engineer has wondered at one time or another if this is the proper thing to do. When facilities and time are available, there is no question but that a thorough study will be made of the effect of changing the speed of load application. A modification of the tension testing machines that has already been quite generally adopted is to equip them with heated jackets so that tension tests can be made at elevated temperatures. Most of these jackets are made in the machine

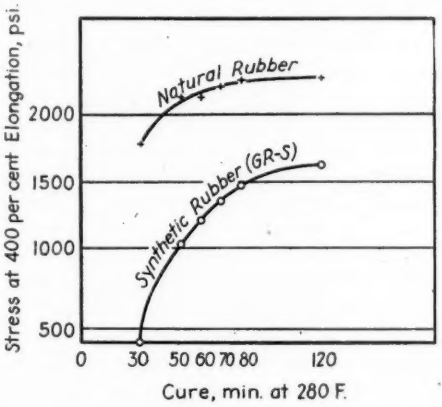

FIG. 3.—Typical curves showing relation of time of cure to tensile stress for tread stocks.

shops of the various companies, and their shape and method of heating vary considerably.

Resilience determinations on natural rubber compounds have been made by a variety of methods, ranging from quite simple ones to some which are complicated and extend over a period of 5 to 6 hours. The early compounds made commercially from synthetic rubber were quite inefficient. By inefficiency is meant incapability of transmitting or absorbing and returning energy. Complicated test machines have not been found necessary for measuring this property. The simplest measure of resilience is the steel-ball rebound test. A steel ball dropped from a definite height will rebound a percentage of the original height, depending on the efficiency of the compound. The disadvantage of this kind of test has been that it is almost impossible to measure the depth the ball penetrates into the compound. A rebounding, swinging pendulum described by Barrett and Mathews[4] lends itself very nicely to resilience testing, not only at normal temperature but also at elevated temperatures, without too much modification. This machine is used extensively at the present time in evaluating synthetic rubber compounds.

The various flexometers can be used in these determinations also, but at present they are employed primarily for a determination of the "heat build-up"

characteristics of synthetic compounds. A definite amount of work is performed on a block of vulcanized synthetic composition by distorting it a definite amount under a controlled compressive force. The work performed on this block may be returned, but some of the energy is transformed into heat during the process of absorbing and returning the energy. The amount of energy so transformed depends on the resilience or efficiency of the compound. If we determine the heat build-up accurately, we then have a reliable measure of the resilience of the compound, and this value is a good criterion of what will happen in service. The Goodrich, St. Joseph, and Firestone flexometers are all recognized in the A.S.T.M. Tentative Methods of Test for Compression Fatigue of Vulcanized Rubber[5]. The Goodyear flexometer has not as yet been included, but there are indications at present that it probably lends itself quite well to the testing of synthetic rubbers. However, the Goodrich machine is in more general use, due to the fact that economically it is the best machine available to evaluate natural rubber vulcanizates. The correct operation of this machine has been described by Lessig[6].

One of the desirable characteristics of synthetic rubbers arises from the fact that air is usually less soluble in them than in natural rubber. This means that gas containers can be made from synthetic rubbers which are more efficient in retaining gas than similar ones made from natural rubber. Barrage balloons that have been constructed as a defense measure and small dive-bomber defense balloons all use gas-retaining films of synthetic rubber, which functions quite well. Also, some day it may be possible to make inner tubes for tires that will retain the air much more efficiently than any of those previously employed. Committee D-11 is now in the process of considering test equipment that lends itself to rapid evaluation of gas permeability. The apparatus in general use at present is the permeameter, supplied by the Cambridge Instrument Co.

Adhesion of synthetic-rubber compositions to metals and other materials is evaluated by the same procedure used for natural rubber as given in the A.S.T.M. Standard Methods of Test for Adhesion of Vulcanized Rubber to Metal[7]. However, measurement of cohesion of the large volume synthetic rubber, GR-S, offers a real problem. One of the first difficulties the process engineer faced when he started to use synthetic rubber compounds was to get them to cohere. Laminations of the same material did not stick together long enough to get them into the curing mould without slippage. Even after they were cured, the various articles and agglomerates had so little cohesion that everyone immediately recognized the low resistance to tear and to deterioration when flexed.

In evaluating this low flex resistance, the DeMattia machine has been used extensively throughout the industry. This machine uses elongation as the distorting force. A tread-groove cracking machine recently developed by Dillon and Prettyman[8] uses both elongation and compression force in sequence to produce flex cracking, which is really loss of particle cohesion. Due to the tendency to take a permanent set, certain synthetic-rubber compounds do not exhibit these cracks as early as similar natural rubber stocks do. However, once the crack starts, whether by stock failure or by an outside force, the crack grows much more rapidly in the synthetic rubber compounds. The cohesion within these synthetic rubber stocks is being improved daily, but at the present time, it can be safely said that, although synthetic rubber is twice as resistant to initial crack appearance, when once the crack appears it grows 40 to 50

times as rapidly as it does in a natural rubber control. Resistance to cutting is therefore a big factor in the service life of a synthetic-rubber stock. Due to the fact that many rubber compositions in service are continually subjected to sharp particles which may produce a small cut, it has been the standard practice of many technologists to introduce before flexing a standard cut in the test sample at the point of flexure. This speeds up the flexing test and also simulates service conditions, because a rubber part is seldom completely shielded from small cuts.

A satisfactory laboratory method for evaluating resistance to cutting has never been developed, although much time and effort has been spent on this problem. Tire test engineers have obtained fairly good results by including a stretch of gravel road in their test fleet course. Unfortunately, this does not lend itself to rubber products other than tires.

In resistance to tearing, some of the synthetic rubbers are especially deficient, particularly at elevated temperatures. There is no one procedure for measuring resistance to tearing that is generally accepted throughout the in-

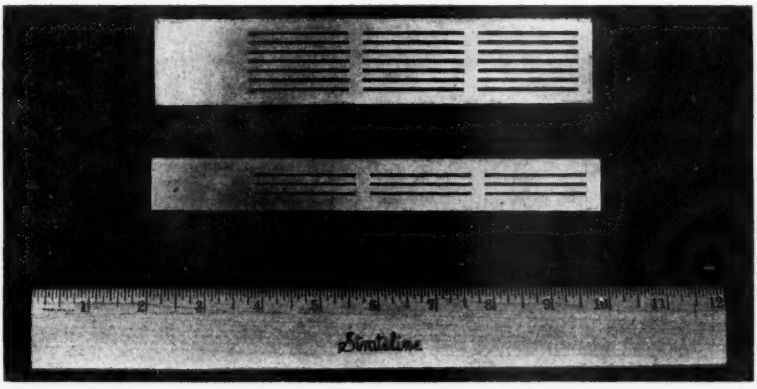

FIG. 4.—Steel inserts used in tearing test.

dustry; in fact, for quite some time, there has been a need for a satisfactory method of evaluating this property. At the Firestone Tire and Rubber Company, use has been made of a heretofore unpublished tear test which will be described in the hope it may be helpful to others. This test consists of stripping apart two slabs of rubber compound which are held together solely by means of connecting rubber fins formed when the slabs are vulcanized under pressure on opposite sides of a slotted metal insert. In the preparation of the specimen, sheets of unvulcanized stocks of essentially the same thickness are placed in a mould, with the slotted metal insert between them so that, during moulding, the rubber stock is forced into the slots, bonding the two slabs together more or less perfectly, depending on the moulding characteristics of the slabs. Different sizes and types of metal inserts may be used similar to those shown in Figure 4. After cure, the specimen is trimmed along the edges of the insert, leaving the stock in the slots as the only bond between the slabs. The rubber tabs at one end of the specimen are then mounted in the grips of an autographic tension testing machine, which are separated at a definite rate while the specimen itself is held at right angles to the direction of pull. In this

way, the rubber fins bonding the two slabs are progressively torn apart along the length of the specimen. Evaluation at elevated temperatures can be obtained by heating the test strips in an oven at a definite temperature for a definite period and then pulling them immediately after removal. The metal inserts help to conduct heat into the center of the slab and stay relatively warmer while the test is being conducted. Further modifications can be used by controlling moulding pressure in a special mould with an air cylinder for pressure. This mould is illustrated in Figure 5. In judging the results obtained, the average pulling force (expressed in pounds) can be used for a comparison as long as the same sizes of inserts with the same size of slots are used. Visual examination of the torn strips shows exactly what property has been evaluated, for when the slabs are perfectly bonded and the tearing occurs at points other than at their junction, the value obtained is a measure of resistance to tearing, but when the separation occurs at the junction, the results are indicative of the bonding characteristics of the slabs used.

The aging characteristics of synthetic-rubber products are not yet well defined, but it seems quite certain that they differ from those of natural rubber. In general, oxidation is considered to play a major part in age deterioration of

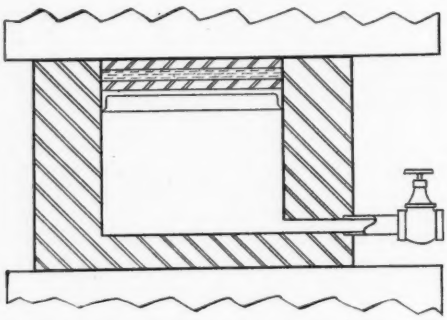

FIG. 5.—Controlled pressure mould.

natural-rubber products, whereas with synthetic rubber it is usually thought that continued polymerization is the principal factor in aging. Correlation of the usual accelerated tests with actual life is of course still impossible, as the use of synthetic rubber is too new. Present practice with synthetic rubber is to subject the vulcanized specimens to exposure in the standard air oven[9], except that the temperature is raised to 100° C instead of 70° C. Oxygen-bomb or oven aging at 70° C produces little deterioration, and there is some evidence that the deterioration starts at about 85° C; hence, the 100° C figure. In discussing aging, attention should be directed to the fact that in the production of synthetic rubbers, especially GR-S, it is necessary to introduce a material which will stop polymerization. For this purpose antioxidants are employed. Accelerated aging tests of synthetic-rubber compounds are therefore tests which evaluate how effectively this antioxidant is functioning and also how long its effect will last. When aging tests are written into a specification, it is well to realize just what the test really is, and act accordingly. Earlier in this paper, it was stated that elongation at break was a property that should be considered carefully. In obtaining aging data, this value is of prime importance, as a decrease in the elongation at break is an indication of a tendency

towards brittleness, and most synthetic rubbers become brittle if polymerization progresses too far.

In contrast to service conditions at elevated temperatures, some rubber products must function at temperatures as low as −70° F, or even lower. Evaluation has been accomplished by placing the test-specimens and apparatus in a cold box or room of sufficient size and capacity to obtain the desired temperature. In this kind of testing, conclusions should not be based entirely on tests made on the article as soon as it reaches the low temperature. Recommendation is made that an exposure period before testing be also considered. There is some indication that crystallization slowly takes place, and continued exposure to this low temperature results in different test data than would be obtained when the test-specimen first reached the low temperature.

Abrasion resistance has always been difficult to evaluate in the laboratory, and all compounders have regulated their thinking by the results obtained from service tests. Committee D-11 has devoted much study to this problem and has adopted the A.S.T.M. Standard Methods of Test for Abrasion Resistance of Rubber Compounds[10]. It is recognized, however, that these methods are only comparative, and that they should not be considered as evaluating service performance. In fact, the limitations are clearly stated in the scope of the standard methods. Few rubber technologists place any reliance on laboratory abrasion figures as an indication of service value, even with natural rubber, and the situation is worse with synthetic rubber compounds because most of these formulas carry high ratios of acetone extractable material which tends to clog and render ineffective small abrasion machines.

Technical Committee A on Automotive Rubber, of the A.S.T.M. Committee D-11 on Rubber Products, functioning under the joint sponsorship of the American Society for Testing Materials and the Society of Automotive Engineers, has developed the A.S.T.M. Tentative Specifications for Rubber and Synthetic Rubber Compounds for Automotive and Aeronautical Applications[11], which catalog under grade numbers the physical properties of a large number of natural and synthetic rubber compounds. In this list of properties are included a none-too-exact hardness figure, values for tensile strength and for elongation at break, and certain aging requirements. In addition, a compression-set value and a load-deflection requirement are specified.

The compression-set value measures the permanent deformation taken by a test-specimen when subjected either to a constant compressive force or when compressed a definite percentage. Both of the methods of exerting compressive force, which are described in the A.S.T.M. Tentative Methods of Test for Compression set of Vulcanized Rubber[12], were in use when natural rubber was available. In the first one, which is designated method A, the compressive force is exerted by a deflected spring which maintains a reasonably constant compressing force on the test-specimen. In the other method, the test-specimens are compressed a definite percentage of their original height, and are held in this position for the duration of the test. The test is run at elevated temperature, although all measurements on the test-specimen are made at room temperature. The results obtained by these two methods are indicative of the service the compound will give at elevated temperatures, and they simulate the two conditions under which rubber is used in many mechanical installations. When the rubber part actually carries a load suspended freely on it, method A is simulated. However, when the part is bolted under compression and held mechanically at a certain deflection, method B gives the best

correlation. The clamps used in these two tests are shown in Figure 6, and the method of using these clamps is obvious. High compression-set results obtained on synthetic rubbers at elevated temperatures have often been erroneously used to rule out compounds which would function very well at lower temperatures. The fact that a certain compound has high flow characteristics at 70° C or higher does not mean that this compound has high flow characteristics at 45° C. Serviceability of synthetic-rubber compounds is so dependent on the temperature at which they operate that it is essential for the evaluation to be made at the service temperature.

The 20 per cent load-deflection characteristic, which is determined according to the A.S.T.M. Tentative Methods of Test for Compression-Deflection Characteristics of Vulcanized Rubber[13], is indicative of the distortion for which allowance must be made when a load is supported by a rubber part. The value

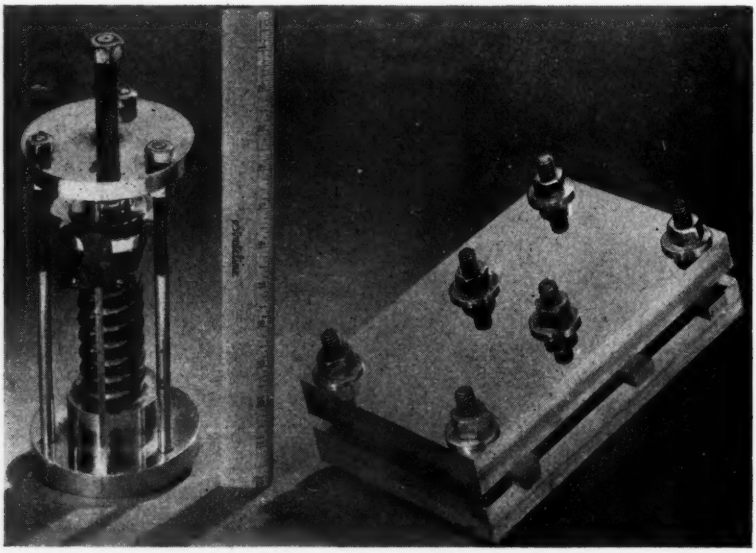

FIG. 6.—Method A and method B compression set clamps.

obtained in the test is the load in pounds per square inch necessary to compress a test-specimen 20 per cent. Using this figure and taking into consideration design factors, it is often possible to estimate the deflection a service load will cause, so that suitable allowance can be made when designing an actual application. This load-deflection characteristic does not take into consideration creep and permanent set, because the results are obtained with rapidly applied loads and immediate readings.

In this paper, discussion of oil absorption tests and methods for evaluating the light-aging characteristics of synthetic rubber has been omitted as somewhat beyond the intended scope. Also, for the same reason, there has been included no discussion of the physical testing of uncured synthetic rubbers, although this is important in the processing factory. No one realizes more than rubber technologists how little is known about the synthetic rubbers on which we are now so dependent. In the present emergency we must push

ahead in spite of this and, at the same time, coöperate in our efforts to improve our knowledge of means for evaluation of their properties. The statement is definitely as true today, as it was the first time the expression was used, "United We Stand and Divided We Fall".

REFERENCES

[1] 1942 Book of A.S.T.M. Standards, Part III, D314–39, p. 447.
[2] Taylor, A.S.T.M. Bulletin No. 123, Aug. 1943, p 25.
[3] 1942 Book of A.S.T.M. Standards, Part III, D412–41, p. 408.
[4] Barrett and Mathews, *Ind. Eng. Chem.* **26**, 1292 (1934).
[5] 1942 Book of A.S.T.M. Standards, Part III, p. 1345.
[6] Lessig, *Ind. Eng. Chem.* **9**, 582 (1937).
[7] 1942 Book of A.S.T.M. Standards, Part III, D429–39, p. 434.
[8] Prettyman, *Ind. Eng. Chem.* **36**, 29 (1944).
[9] 1942 Book of A.S.T.M. Standards, Part III, D573–42, p. 420.
[10] 1942 Book of A.S.T.M. Standards, Part III, D394–40, p. 439.
[11] 1943 Supplement to Book of A.S.T.M. Standards, Part III, D735–43T, p. 416.
[12] 1942 Book of A.S.T.M. Standards, Part III, D395–40, p. 1339.
[13] 1942 Book of A.S.T.M. Standards, Part III, D575–40T, p. 1336.

CURE OF GR-S IN THICK ARTICLES *

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Information on the relative rates of cure of GR-S stocks and similar Hevea stocks in thick sections is of interest to many rubber manufacturers. Since curing conditions for thick articles from Hevea stocks have been established, they would like to know how these conditions must be altered when GR-S stocks are used in the same applications. They could develop a GR-S stock with the same rate of cure as the Hevea stock which it replaces according to laboratory tests on comparatively thin sheets, but this agreement does not mean necessarily that thick sections cure at the same rate. The respective rates of heat flow through the rubbers must be considered. Only if the rates of heat flow as well as the curing rates of thin sections are in agreement, will the curing rates of the thick sections be equal.

Juve and Garvey[1] found that GR-S tread stocks cure faster in the center of thick sections than similar Hevea tread stocks. They were unable to explain this behavior because, according to their measurements, the thermal conductivity of the GR-S tread stock was less, and its specific heat greater than, the corresponding values for the Hevea tread stock. They concluded that the difference may be due to an exothermic reaction.

Incidental to the development of cures for thick articles such as caisson gaskets, the authors have investigated the relative curing rates of GR-S and Hevea tread stocks. The rates of cure on the outside and in the center of 0.25-inch and 2-inch thick round slabs were found at 275°, 290°, and 305° F, and temperature measurements were made in 2-inch thick round slabs during and after cure. The recipes for the tread stocks are given in Table I. The tensile properties of these stocks, measured on 0.05-inch thick sheets cured for various times at 290° F. are graphed in Figure 1. The GR-S stock cured more slowly than the Hevea stock in thin sheets.

TABLE I

RECIPES

	GR-S stock	Hevea stock
GR-S	100.0	...
Smoked sheet	...	100.0
Channel black	50.0	50.0
Zinc oxide	3.0	3.0
Rosin oil	5.0	...
Stearic acid	...	3.0
Pine tar	...	3.0
Phenyl-α-naphthylamine	...	1.0
Mercaptobenzothiazole	1.5	1.35
Diphenylguanidine	0.3	...
Sulfur	2.0	2.75

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 36, No. 7, pages 649–653, July 1944.

DETERMINATION OF RATE OF CURE

The modulus at 300 per cent elongation was used for establishing state of cure on the 0.25-inch and 2-inch slabs. The curing times required to reach a modulus of 1000 pounds per square inch for the GR-S stock and of 1200 pounds for the Hevea stock were regarded as a measure of the respective rates of cure. These moduli corresponded to about the best technical cures from the standpoint of tensile properties.

The 0.25-inch and 2-inch slabs were built up before cure by plying together 0.050-inch layers of stock. The layer on the bottom and the layer in the middle of the stack were dusted with soapstone so that they could be separated easily

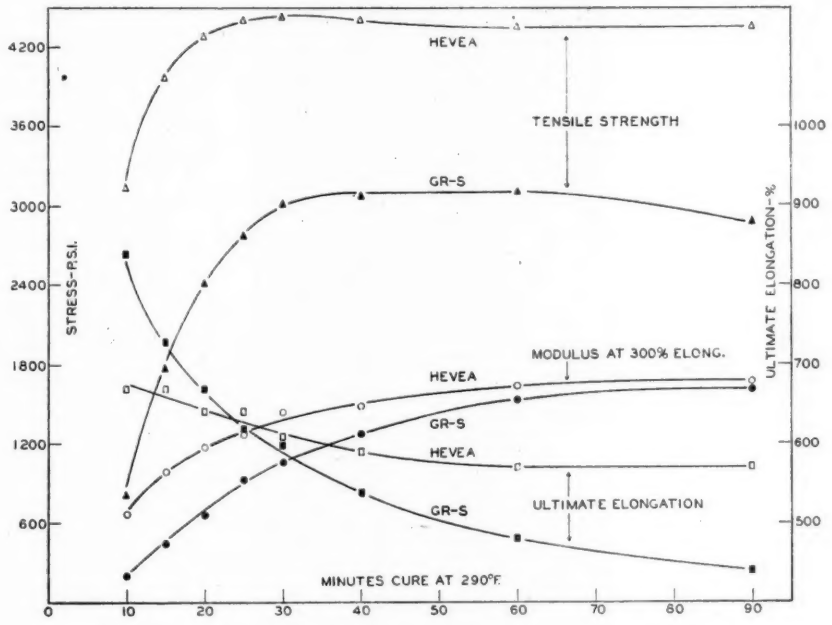

FIG. 1.—Range-of-cure data at 290° F on tread stocks molded as 0.05-inch sheets.

from the rest of the slab after cure. Figure 2 illustrates the laminations after cure on a 1-inch slab which was used in preliminary tests.

The direction of the grain was marked on the bottom and middle layers before cure. After cure the layers were separated, and eight tensile specimens, A.S.T.M. type C, were died out with the grain from the bottom layer and also from the middle layer. The modulus values for each layer were averaged.

The diameter of the 0.25-inch and 2-inch slabs was 13 inches. The eight tensile specimens were died out so that none was closer than 2 inches to the edge of the slab. Thus, all of the heat for the vulcanization of these specimens came from the end plates, since the end plates were closer than the wall of the circular mould to the locations from which the tensile specimens were taken.

The important time intervals observed in this testing program follow: not less than 16 hours between mixing and calendering for both stocks, 4–24 hours between calendering and curing for the GR-S stock, 16–30 hours between

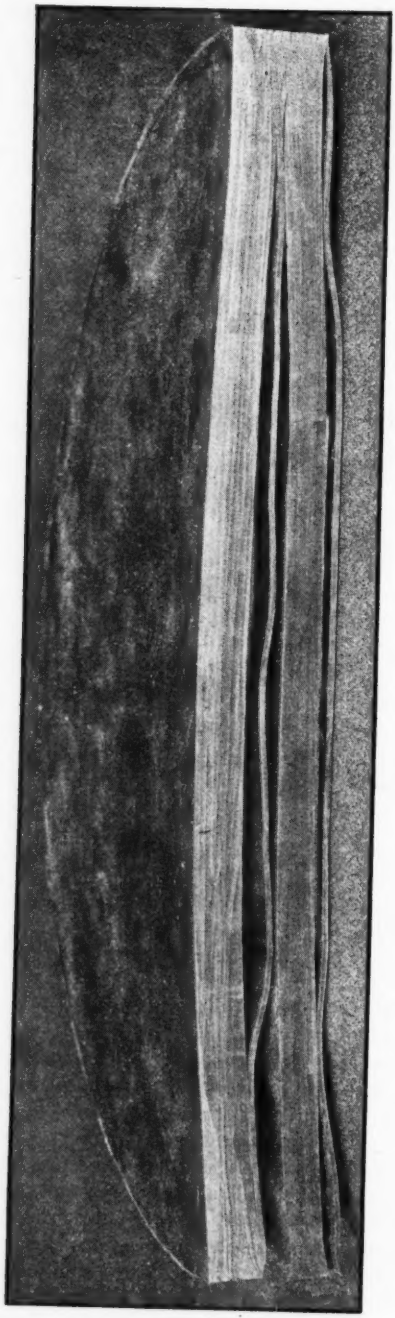

FIG. 2.—Laminations after cure in 1-inch slab, used in preliminary tests.

calendering and curing for the Hevea stock, 72–96 hours between curing and testing for both stocks. The stocks were conditioned at 82° F during the intervals between operations. Before curing, the hydraulic press platens were adjusted to the desired temperature within ±0.5° F by means of a thermometer block. Tensile testing was done at 82° ± 5° F.

A graphical method was used for finding the times of cure to reach the critical moduli. A typical graph is shown in Figure 3. At least two points

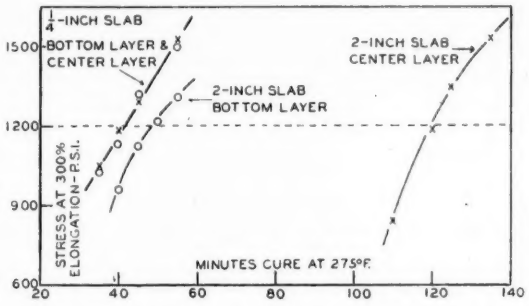

FIG. 3.—Typical relations between time of cure and modulus in bottom and center layers of Hevea tread-stock slabs cured at 275° F.

were obtained below and two points above the critical modulus for every curve so that the point of intersection of the curve with the modulus line could be established accurately. Figure 3 shows that the bottom layer and the middle layer of the 0.25-inch slab cured apparently at the same rate; this held true for the 0.25-inch slabs from both stocks at the three temperatures. The times to reach critical moduli in the 0.25-inch and 2-inch slabs at the three temperatures are listed in Table II.

TABLE II

CURING TIMES TO REACH CRITICAL MODULI (BEST CURE)

Tread stock	Curing temp. (° F)	Minutes to Reach Critical Modulus: 0.25-in. slab, average of bottom and center layers	2-inch slab: Bottom layer	2-inch slab: Center layer
GR-S	275	52.5	60	118.5
	290	30.5	39	96
	305	17.5	23.5	80
Hevea	275	41.5	49	120.5
	290	23.5	0.5	99
	305	14.5	20	85

DEGREE OF OVERCURE ON SURFACE

The data in Table II are in agreement with the observations by Juve and Garvey regarding the relative rates of cure of GR-S and Hevea stocks in thick articles. The times to reach best cure in the center of the 2-inch slabs were slightly less for the GR-S stock, even though the Hevea stock cured faster on the outside layer of these slabs and also in the 0.25-inch slabs. The data demonstrate that thick articles of this GR-S stock can be properly cured with

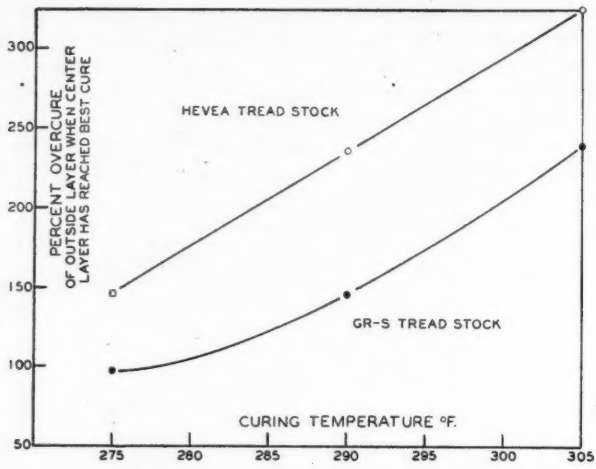

FIG. 4.—Effect of curing temperature on degree of overcure of a 2-inch slab.

less overcure for the stock located near the surface than in the case of thick articles of the Hevea stock.

Figure 4 shows this more clearly. The curves are based on the assumption that the actual time of cure beyond the best cure may be regarded as a measure of the extent of overcure. The curve for the Hevea stock is above that for the GR-S stock; this shows that the outer layers of the Hevea stock were more over-cured than the outer layers of the GR-S stock when the respective center layers reached the respective critical moduli.

TEMPERATURE MEASUREMENTS

The next problem was to find why a GR-S tread stock cures relatively faster in a thick section than a similar Hevea tread stock. The explanation offered by Juve and Garvey can be easily tested by making temperature measurements in the rubber under suitable conditions. It was decided to conduct experiments along this line.

A 4-inch diameter, 2-inch thick mould was made, with holes drilled at two diametrically opposite points through the side to accommodate No. 26 thermo-

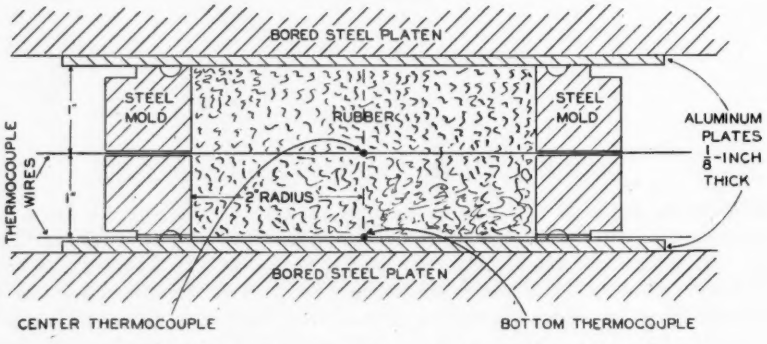

FIG. 5.—Cross section of assembly used in heat flow experiments.

couple wire. The holes were centered with respect to the faces of the mould. Notches to accommodate the wire were made at diametrically opposite points on one face of the mould.

The appearance of the assembly during cure is shown in Figure 5. The center thermocouple was located far enough in from the side of the mould so that the temperature of the thermocouple would not be affected appreciably

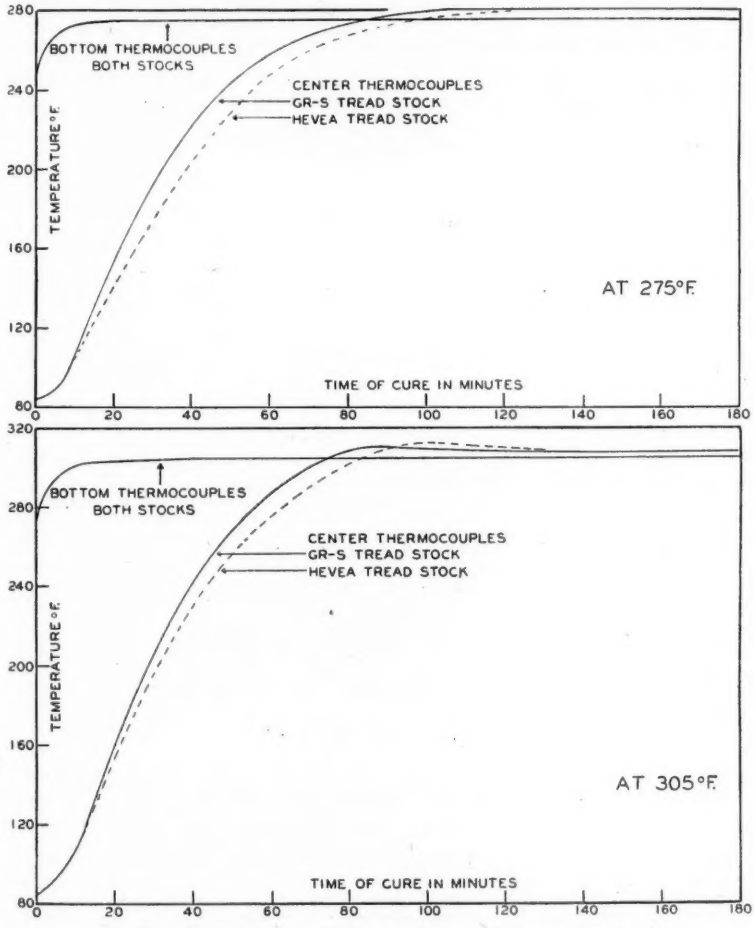

FIG. 6.—Temperature rise in 2-inch slabs at 275° and 305° F.

by heat flowing along the wire. Moreover, it was considered that the temperature of the thermocouple would not be affected by heat flowing in from the side of the mould through the rubber because this distance was twice the distance to the faces of the mould. It could be safely assumed, therefore, that all of the heat reaching the center thermocouple came through the rubber from the faces of the mould.

The procedures for preparation and test were as follows: The cold mould was placed on the cold bottom plate with the bottom iron-constantan thermo-

couple in position. A disk of raw stock, slightly over 1 inch in thickness and slightly under 4 inches in diameter, was placed in the mould. The center iron-constantan thermocouple was placed in position on top of this disk, and another disk of raw stock with similar dimensions was placed on top of the thermocouple. The cold top plate was placed in position, and the entire assembly put into the hydraulic press which had previously been brought to the correct

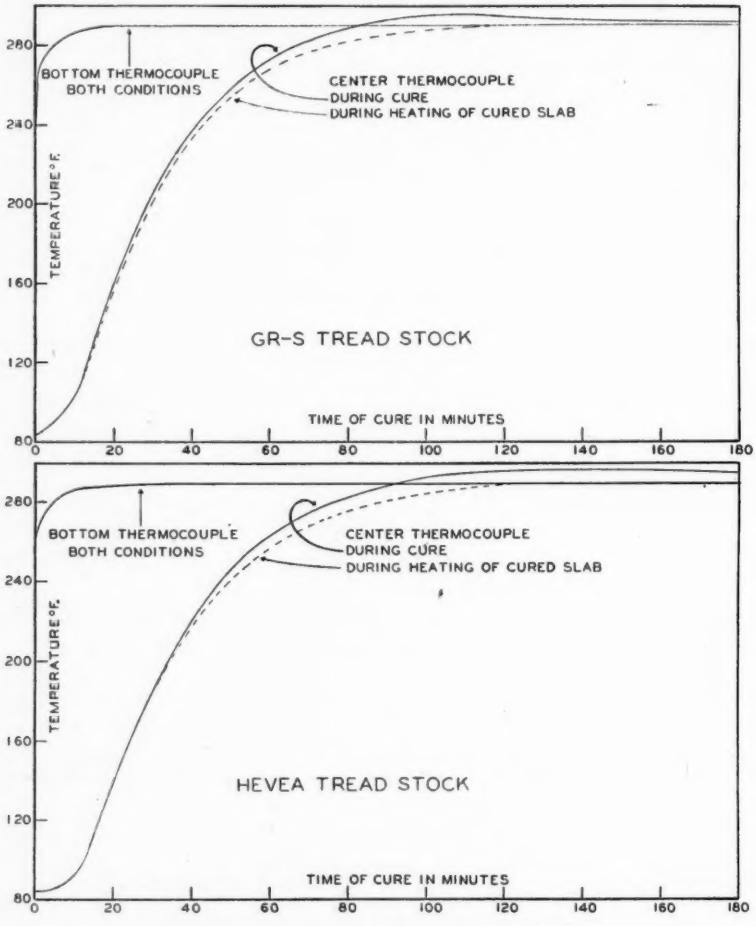

FIG. 7.—Temperature rise in 2-inch slabs at 290° F.

temperature. The press was closed at once, and the time measurement with a stopwatch was started. The rise in temperature of the thermocouples was followed with a potentiometer. After the temperature of both thermocouples had leveled off, the cure was discontinued, and the rubber was cooled. The rubber specimen was then cut open to determine the actual location of the center thermocouple. The center thermocouples in all slabs were found to be within 0.02 inch of vertical center.

It was assumed that the cold aluminum plates attained the curing temperature almost immediately, and that the cold mould had little or no effect on the temperature rise of the thermocouple because the intermediate rubber provided adequate insulation.

The temperature rise data for cures at 275° and 305° F are plotted in Figure 6. The data for the cures at 290° F gave similar curves. These curves show that the center of the slabs reached the curing temperature much more slowly than did the outer surfaces. Of more significance, they also show that the rates of temperature rise at the centers of the GR-S slabs were faster than the rates at the centers of the Hevea slabs; and that the temperatures at the centers of all slabs rose above the respective curing temperatures.

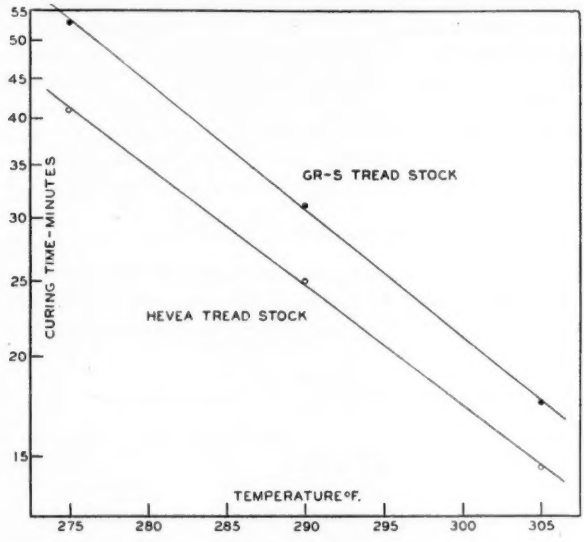

FIG. 8.—Curing time *vs.* temperature (curing time equals time to reach critical modulus).

EXOTHERMIC REACTIONS

The difference in rates of temperature rise explains why thick articles of GR-S stocks cure relatively faster than thick articles of similar Hevea stocks. It does not appear that the faster rate of temperature rise of the GR-S stock could be due to an exceptional heat generation in this stock, as suggested by Juve and Garvey, because the center temperatures of both stocks exceeded the respective bottom temperatures by about the same amount. The peak values of the differential temperatures follow:

Curing temperature (° F)	Maximum temperature rise (° F)	
	GR-S	Hevea
275	5	5
290	5	7
305	5	7

These differential temperatures were due to exothermic reactions between sulfur and the respective rubber hydrocarbons which have been investigated[2].

That no exceptional exothermic reaction occurs during the vulcanization of the GR-S tread stock was definitely proved by the following experiments:

A 2-inch slab of the GR-S tread stock was vulcanized at 290° F in the assembly depicted in Figure 5. The temperature rises during vulcanization were followed, and the cure was continued until the temperature of the center thermocouple dropped to the temperature of the bottom thermocouple, an indication that exothermic reaction had stopped. The total curing time was 220 minutes. The assembly was then withdrawn from the hydraulic press and cooled. When the slab had reached a uniform temperature of about 80° F throughout, the assembly was again placed in the hydraulic press at 290° F, and the rise in temperature of the two thermocouples was followed. The temperature rises during cure and during the second heating are plotted in Figure 7 for both stocks. The time for the Hevea tread stock to pass through the exothermic reaction was 370 minutes.

The curves for both stocks are similar. The bottom thermocouples soon attained curing temperature at both heatings; the center thermocouples surpassed the curing temperature during the original cure, but leveled off at the curing temperature during the second heating, due to the absence of further exothermic reaction. There was no evidence that an exceptional exothermic reaction occurred in the GR-S stock. The relatively faster cure of thick GR-S articles must be due simply to the faster thermal diffusivity in these stocks.

THERMAL DIFFUSIVITIES

The curves may be used for calculating the thermal diffusivities of the stocks. Data were obtained according to the method described by Williams[3], and are presented in Table III. In every case the thermal diffusivity increases as the

TABLE III
THERMAL DIFFUSIVITY OF TREAD STOCKS

	Diffusivity (sq. in. per min.)			
	290° F Cure		290° F Reheat	
	GR-S	Hevea	GR-S	Hevea
At 120° F	0.0140	0.0124	0.0138	0.0117
At 260° F	0.0169	0.0144	0.0162	0.0140
Av., 80–290° F	0.0152	0.0131	0.0149	0.0128
Calculated by Juve and Garvey[1]			0.0118	0.014

temperature of the rubber rises. The average diffusivities of the GR-S stock are higher than the average diffusivities of the Hevea stock. The diffusivities during actual cure are higher than the diffusivities during reheat of the cured slabs, probably as a result of heat generated in the exothermic reactions. Both cure and reheat data indicate that the GR-S stock has higher diffusivity than the Hevea stock.

The last relation contradicts the diffusivity data given by Juve and Garvey, calculated from thermal conductivity and specific heat measurements. Their data show that the diffusivity of a Hevea tread stock is 19 per cent greater than that of a GR-S tread stock. The data obtained in this work indicate that the diffusivity of the GR-S tread stock is 16 per cent greater than that of the Hevea tread stock. No explanation is offered for this difference.

TEMPERATURE COEFFICIENTS

From the data on modulus *vs.* time of cure for the bottom layer of the 0.25-inch slabs, as exemplified in Figure 3, it was possible to calculate values

for the respective temperature coefficients of vulcanization over the range 275° to 305° F. The semilogarithmic plot of curing time *vs.* temperature is presented in Figure 8. The temperature coefficients of vulcanization for 10° F intervals were calculated to be 1.45 for the GR-S and 1.41 for the Hevea tread stock. The former agrees well with the value of 1.47 calculated from information given by Juve and Garvey[1]. The latter agrees well with the value of 1.39 found by Morris[4] for a pure gum Hevea stock accelerated by mercaptobenzothiazole.

REFERENCES

[1] Juve and Garvey, *Ind. Eng. Chem.* **36**, 212 (1914).
[2] Blake, *Ind. Eng. Chem.* **26**, 1283 (1934); Bruce, Lyle and Blake, *Ind. Eng. Chem.* **36**, 37 (1944).
[3] Williams, in "Vanderbilt 1932 Rubber Handbook", R. T. Vanderbilt Co., New York, p. 83.
[4] Morris, *Ind. Eng. Chem.* **25**, 1400 (1933).

THE DU PONT MODIFIED WILLIAMS PLASTOMETER *

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Webster defines plasticity as "the ability to retain a shape attained by pressure deformation". Plasticity measurements are made by rubber technologists for one or more of the following reasons: (1) to measure the workability of rubber or synthetic elastomers; (2) to determine the effect of natural or accelerated aging on the processability of compounded rubber or synthetic elastomers; (3) to determine to what extent softeners or compounding ingredients may have affected the workability of rubber or synthetic elastomers; (4) to serve as a control test in the manufacture of synthetic elastomers.

The Williams Plastometer has been widely used in the rubber industry for a number of years. Since its introduction in 1924 by Williams[1] it has undergone a number of refinements[2] which have improved its mechanical efficiency and simplified its operation. However, the fundamental operating principles of this machine have been retained.

This article discusses the modifications that have been incorporated into the instrument now in use at the du Pont rubber laboratories.

DESCRIPTION OF THE INSTRUMENT

Figure 1 shows one of the first Williams plastometers that was used in the du Pont rubber laboratory at Deepwater, N. J. This instrument, which is still available, is a simple device that induces a dead-weight load of five kilograms on a pellet of constant volume (2 cc.) between two parallel plates (4.5 by 4.5 inches). The dial gauge indicates the thickness of the pellet as it is being compressed. This plastometer was operated at a given constant temperature (100° C), and dial gauge readings were taken at specified intervals of time (three, five, and ten minutes). From these data Williams plotted thickness-time curves which conformed to the general equation of the form $Y = KX^n$, where Y equals the thickness of the pellet in millimeters and X equals the time in minutes. From experimental data n was found to be -0.196, giving $K = YX^{0.196}$, where K is called an index to the plasticity of the sample.

Experience has shown that it is unnecessary to plot the thickness-time curve, and, as will be discussed later, the normal measurement of plasticity is expressed as the thickness of the pellet in thousandths of an inch after three minutes' compression. It has been found also that the recovery of the elastomer is an important measure of processability, and this factor expressed as the increase in thickness after one minute's storage at room temperature is usually made at the conclusion of the plasticity determination.

Figures 2 and 3 show the presently used du Pont modified Williams plastometer installed in its especially designed hot air oven.

Figure 4 is a schematic sketch of this plastometer, which consists primarily

* Reprinted from the *India Rubber World*, Vol. 110, No. 2, pages 174–175 and 181, May 1944.

of a scale balance that has a capacity of 15 pounds and a sensitivity of 20 grams. This balance is so weighted that it produces a load of five kilograms on the test pellet. The knife edges of the lever mechanism, which is shown in Figure 4, produce not only a minimum of friction, but also permit the movable platen to remain truly parallel to the fixed platen throughout its vertical travel. The brass cams which are used to actuate the movable platen in the loading and unloading of the test pellet are fast-acting, and are controlled from the exterior on the right side of the oven. To make the operation of the plastometer less cumbersome, the size of the platens used on the original apparatus was reduced and changed in shape to disks ($2\frac{1}{2}$ inches in diameter and $\frac{1}{2}$-inch thick).

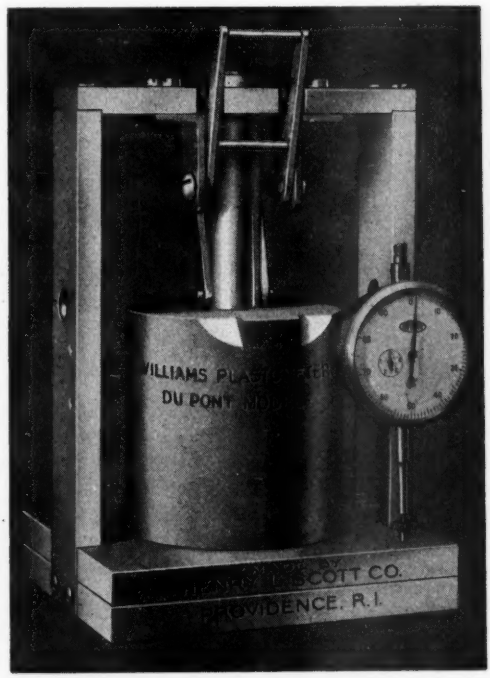

FIG. 1.—Original Williams plastometer, du Pont model.

The dial gauge, which has jewel bearings, is mounted rigidly to the frame that supports the fixed platen, and is actuated by an adjustable arm that is an integral part of the movable platen. Thus the distance between the platens is indicated at all times.

Directly above the platens is the conditioning shelf, which consists of two rectangular bars separated by spacer bars 0.4-inch in thickness. The lower bar is fixed, but the upper bar is movable. The movable bar, which is on loose fitting dowels, may be lifted vertically by means of the lever mechanism shown in Figure 4, and is operated from the exterior of the oven on the right side.

The oven is simply constructed of Transite and metal parts assembled with bolts and machine screws, making the interior of the oven readily accessible

if repairs become necessary. The oven is mounted on Neoprene sponge to dampen out vibrations that would affect the accuracy of the test results if transmitted to the plastometer. Circulation of the air in the oven is produced by two six-inch fans. One fan is adequate for operation of the oven, but the two are installed to insure continued operation if one fan motor should fail. The air enters the oven on the lower right-hand side of the working chamber and exits through orifices at the bottom and top of the left-hand side. The air is then circulated over electrical heating elements located above the working chamber and enters at the bottom on the right-hand side, thus completing the cycle.

The temperature of the oven is controlled by a DeKhotinsky bimetallic thermoregulator within the oven, which is connected through a mercury relay

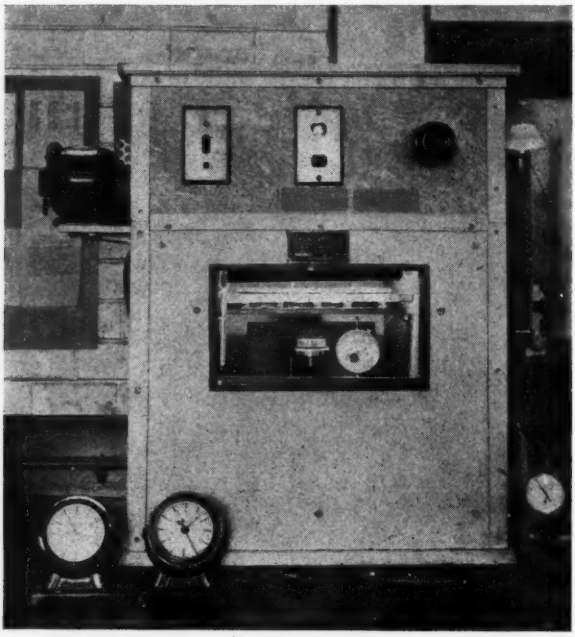

FIG. 2.—Modified du Pont Williams plastometer in specially designed hot air oven.

to the heating elements. A thermometer located on the left side of the oven in front of the conditioning shelf indicates the temperature.

The efficiency of the oven is improved considerably by having a vertically sliding window instead of a door which would sweep hot air from the oven each time the platens were loaded and unloaded. This window is mounted on brass door runners, and is counterweighted. The window is constructed of two plates of Tuf-Flex glass (Hires Turner Co.), separated by a dead air space which is the insulating medium.

PREPARATION OF TEST PELLETS

Immediately after being milled, the raw or compounded elastomer is plied up to a thickness of $\frac{5}{8}$ to $\frac{3}{4}$ inch. Special care is taken to prevent trapping air between the plies. Three pellets are prepared for each test. They are

punched out in a clicking machine, using a special die which produces a pellet having a volume of two cubic centimeters. The die was developed many years ago at the Miller Rubber Co. by Raymond Warner. The pellets are dusted lightly with soapstone, and stored in a metal U clip in such a manner that the pellets are held to a height of approximately 0.40 inch during storage prior to testing.

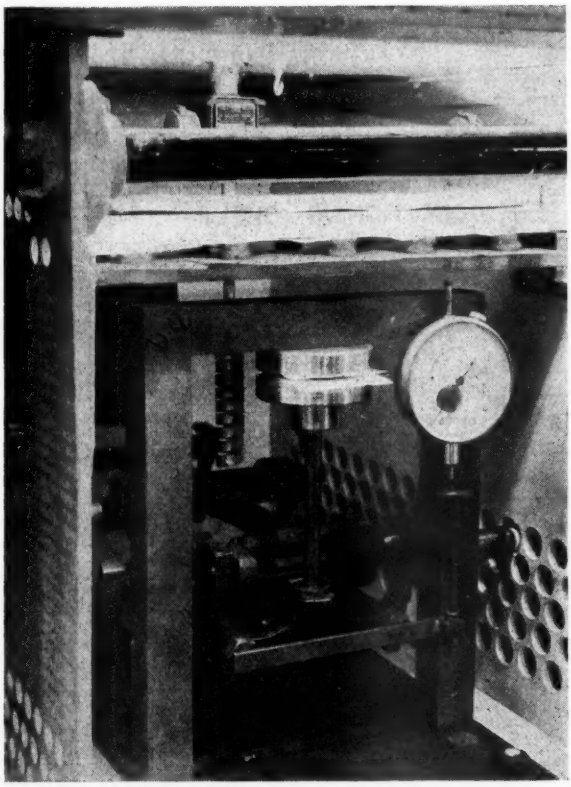

FIG. 3.—Closeup of modified du Pont Williams plastometer.

METHOD OF DETERMINING PLASTICITY

Although plasticity measurements may be made over a wide range of temperatures, the du Pont laboratories have selected 80° C as the temperature of broadest interest. The oven temperature is controlled to $\pm 1°$ C. The test pellets are removed from the metal U clip, put between two sheets of onion-skin paper, and then placed on the conditioning shelf in the oven for 15 minutes. Here the pellets are compressed before testing to a standard height of 0.4 inch while they are being heated to $80 \pm 1°$ C. Individual pellets in a series for test are placed on the conditioning shelf at three-minute intervals to permit continuous operation. The zero point of the dial gauge is checked by placing two pieces of onion-skin paper between the clean platens, applying the load, and setting the gauge at zero. The plastometer is now ready for use.

At the end of the 15-minute conditioning period the pellet is placed in the center of the lower platen, and the load of five kilograms applied. After the load has been applied for three minutes (measured by a stop-watch) the dial reading, which indicates the thickness of the test-specimen in thousandths of an inch, is recorded as the plasticity figure, and the pellet is immediately removed from the plastometer. The pellet is allowed to cool for one minute at room temperature (82° F), and then the average thickness of the compressed pellet, still between the two papers, is measured. A Randall-Stickney dial gauge, equipped with a foot 0.25 inch in diameter and a three-ounce weight,

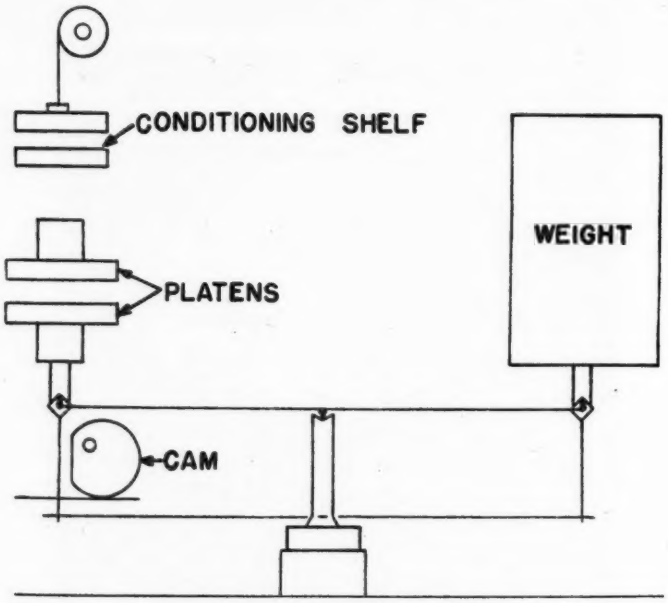

FIG. 4.—Schematic sketch of mechanism of modified du Pont plastometer.

is used to measure the thickness of the cooled pellet. The measurement is made by taking an average of the readings obtained in the circle whose radius is approximately one-half the radius of the compressed pellet. This figure in thousandths of an inch is recorded as the recovery figure. The difference between the recovery figure and the plasticity figure is known as the recovery. To insure continuity of operation, two stop-watches are used in the running of this test, and extreme care is exercised in the timing and manipulation of the plastometer.

Pellet No.	Plasticity figure	Recovery figure	Recovery
1	117	125	8
2	118	125	7
3	117	124	7
4	117	125	8
5	118	125	7
6	117	124	7

The reproducibility of test results obtained with the modified Williams plastometer is shown by the following data. Test pellets were taken from a batch of uncompounded Neoprene Type GN (GR-M), following a mechanical breakdown for six minutes on a 30-inch mill. The surface temperature of the rolls was 70° C, and the distance between the rolls was 0.060 inch.

Under normal conditions only two pellets are used for each test, but if the plasticity or recovery figures of the two pellets do not check within 5 per cent, the third pellet is tested.

REFERENCES

[1] Williams, *Ind. Eng. Chem.* **16**, 362 (1924).
[2] De Vries, *Arch. Rubbercultuur* **8**, 223 (1925); van Rossem and van der Meijden, *Rubber Age* (N. Y.) **23**, 438 (1928).

THE TESTING OF RUBBER IN COMPRESSION *

C. M. Blow and W. P. Fletcher

With the increased use of rubber as an engineering material, considerable attention has to be paid to the characteristics of natural and synthetic rubbers in compression. For oil seals, in particular, what is loosely termed permanent set of the rubber must not be so great as to lead to breakdown of efficiency.

Up to the present the need for laboratory evaluation of different rubbers for this property has been met by tests which involve measuring the dimensional changes in a test-piece subjected to a constant strain or stress for a certain time and then allowed to recover for a certain time.

Although it gives some indication of behavior, this method of test suffers from the great disadvantages that the time factor is arbitrary and the change of dimension is measured, whereas in service the dimension of the rubber is maintained virtually constant by the rigid members of the system. In other words, in the case of a sealing ring on a piston working in a cylinder, the effectiveness of the seal depends, in large measure, on the pressure exerted by the rubber on the cylinder wall. As this pressure decays, so, it is believed, the sealing efficiency decreases.

The following apparatus of very simple construction, as indicated in the diagram (Figure 1), was devised to observe the decay of stress in a sample of rubber compressed to a constant strain.

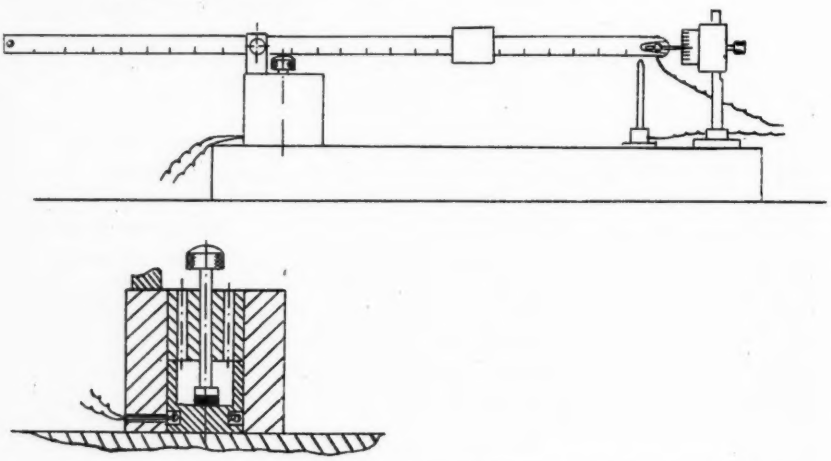

Fig. 1.—Testing machine for rubber in compression at constant strain immersed in oil.

A pellet of known dimension (⅜–½ inch diameter by ¼–½ inch thick is suitable) of the compound to be tested, contained in a bath, is compressed to a strain of the required percentage by means of a plunger depressed by a lever

* Reprinted from the *India-Rubber Journal*, Vol. 106, No. 15, pages 403–404, April 8, 1944.

arm carrying movable weights. The load necessary to maintain the percentage compression is measured from time to time by moving the weights until the lever arm just breaks contact with a stop arranged to prevent any strain in excess of the required percentage. This contact is indicated by a simple electric lamp circuit. After each measurement the weights are arranged so that the lever arm is resting heavily on the stop, thus ensuring that the percentage compression is maintained until the next reading is taken.

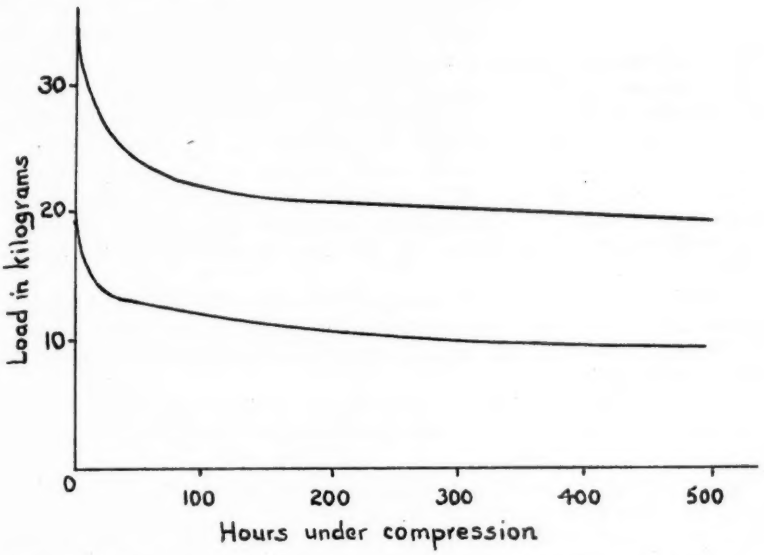

FIG. 2.—Curves showing decay of stress in two synthetic-rubber mixtures of different quality but of the same hardness, at a constant strain of 30 per cent compression. Pellet size 0.375 inch diameter and 0.25 inch thick.

The bath containing the sample under test is arranged so that it can be maintained at any required temperature and the fluid in the bath can be an inert one, such as glycerine or an oil, where the conditions of service demand it.

The decay of stress can be plotted against time and accurate comparisons made between compounds. Figure 2 gives typical curves obtained on two synthetic qualities which, although of the same Shore hardness, give different stresses at the same compression.

ACKNOWLEDGMENT

The authors express their thanks to the laboratories of the John Bull Rubber Co., Ltd., for permission to publish this note, and to W. P. Smith, Chief Chemist of Automotive Products Co., Ltd., for assistance with the development of the apparatus.

ERRORS ARISING IN THE PENDULUM TEST FOR RESILIENCE OF RUBBER *

D. BULGIN

The resilience of rubber is usually measured by a rebound test, and an accurate instrument for this purpose is the rebound pendulum. This instrument consists of a compound pendulum with a steel ball, fixed at the center of percussion, which strikes a rubber sample held in a suitable holder. The pendulum is released from a known angle, and the rebound angle is measured. The ratio of energy of rebound to energy of fall is the resilience value of the rubber. The distance the ball indents the rubber also can be measured, and under certain defined conditions can be used to determine the hardness of the rubber.

An account of the pendulum used by the Dunlop Rubber Co., Ltd., is given by Jones and Pearce[1], and descriptions of similar instruments derived from the Fort Dunlop pendulum and used by American manufacturers are given in various publications[2].

The instrument is capable of a high degree of accuracy, and angles can be read to 3 minutes of arc or less, giving a maximum error due to this cause on one reading of 1 part in 500.

The purpose of this paper is to describe certain refinements in the technique of using the pendulum to improve the precision of the instrument.

It is essential that the mechanical construction of the instrument, particularly the rigidity of the pendulum and its supporting column and the location of the striking ball at the center of percussion, shall be precise.

Resilience measurements.—Experience shows however that, even when these conditions are achieved, there are systematic deviations from a constant value of resilience for the same rubber sample with change of the angle through which the pendulum falls on to the sample and with variation in the method of securing the rubber sample in the holder. It is of importance to know whether these are due to real variations of the resilience of the rubber with amplitude of indentation or whether they are due to energy losses apart from those caused by internal friction in the rubber.

The possible sources of energy loss are air-damping of the pendulum, loss of energy due to movement of the back of sample against the supporting plate, loss of energy due to movement of the ball on the front surface of the sample, and vibration of the pendulum and its supporting column.

All these causes make the observed resilience lower than the true value, and, as air-damping losses increase as a power of the pendulum velocity, these cause resilience to decrease with increase in pendulum energy.

The decrease in resilience which takes place with increased pendulum energy of fall is shown in Figure 1. The standard method of testing includes errors due to all four sources given above. The first step was to eliminate the second

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 20, No. 1, pages 24–29, June 1944. This paper was presented before the Midland Section of the Institution of the Rubber Industry at its meeting in Birmingham, July 26, 1943.

of these, the loss of energy at the back of the sample, by bonding the sample to a metal plate so that no movement relative to the metal could take place and so frictional loss at the back of the sample would be eliminated. The reduction of loss of energy is quite appreciable, as is shown by the rise in the resilience values (Figure 1).

In Figure 2 these resilience values are translated into energy loss values, and the calculated values of loss of energy due to air-damping of the pendulum have been included on the graph.

By subtracting the calculated value of air-damping from the loss measured when the sample is bonded to a metal backing plate, any difference can be ascribed to vibration of the pendulum and its supporting column and to loss of energy due to movement of the ball on the front surface of the sample. It

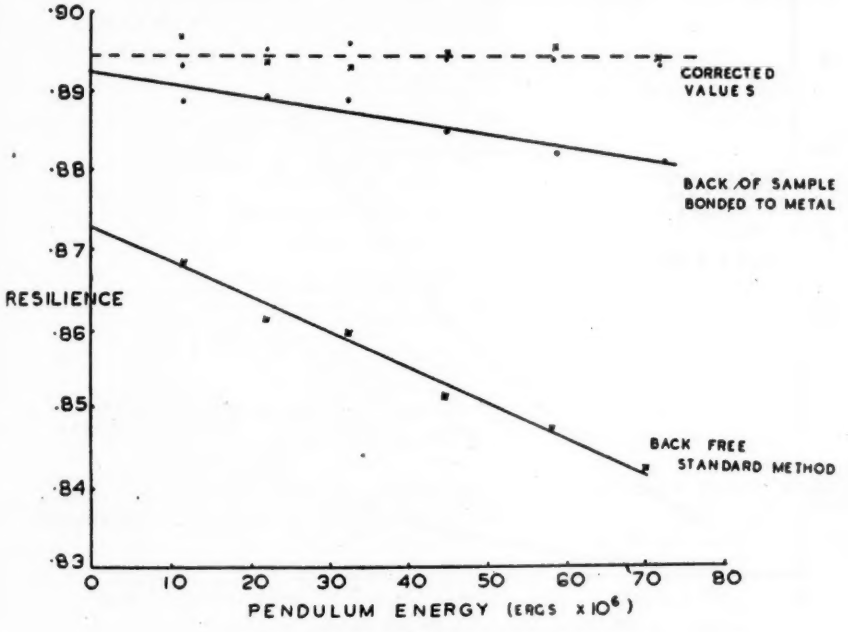

FIG. 1

will be seen from Figure 2 that the difference is very small, and by repeating this experiment on several samples of different resilience, which, due to the different heights of rebound had different air-damping losses, it was established that the energy losses by movement of the ball on the surface of the sample and the vibrations of the pendulum and its support were so small as to be negligible compared to the losses due to air-damping of the pendulum.

However, after making allowance for the air-damping losses and showing that movement of the ball and vibrations of supports are negligible sources of energy loss, it is found that substantial losses still occur when the back of the sample is free to move over the supporting plate (Figure 2).

As the sides of the sample are free from constraint, the energy-loss must be due to losses occurring at the back of the sample, due to movement of the sample on its supporting plate when struck by the pendulum ball. This loss is several

times greater than the air-damping losses, and for a rubber of resilience 0.90 is about 30 per cent of the internal energy loss in the rubber.

The movement of the back of the square sample when indented by the ball is complex, but a check on the value of the loss has been made by the following method. The energy loss at the sample-supporting plate interface is caused by the product of movement of the rubber and the pressure with which it is pressed on to the supporting plate. As the coefficient of friction of clean dry rubber is not appreciably dependent on the type of compound used, and as the stress-strain curves for rubbers are roughly of the same type though differing in magnitude, it is to be expected that the energy loss will be some function of

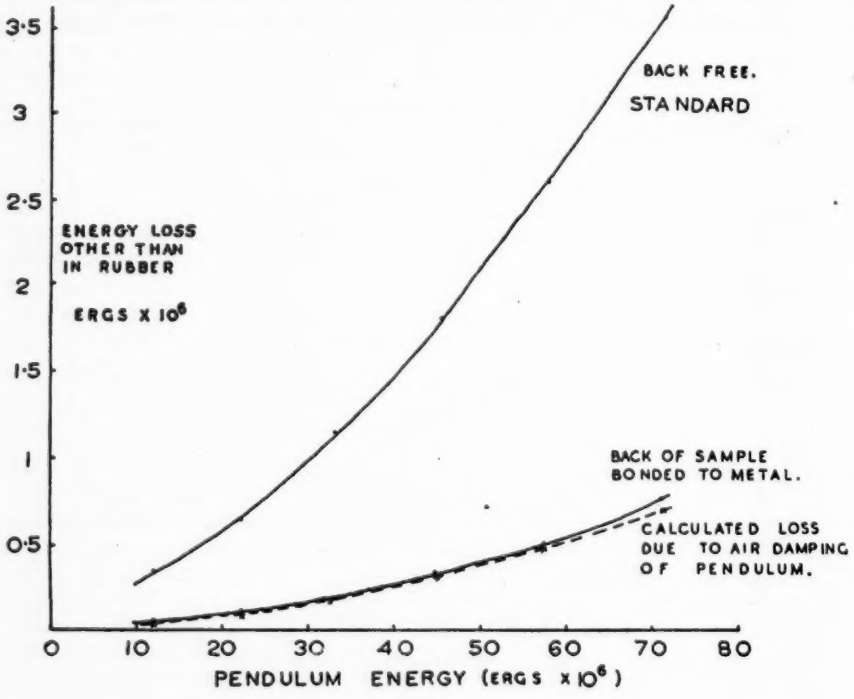

FIG. 2

the maximum pressure at the center of the block and the indentation of the ball into the rubber.

The values of these two factors can be calculated from the experimental law connecting indentation and pressure, which is $p = k\,s^x$, where p is the pressure, s is the indentation, and k and x are constants for any one sample. From this it can be shown that $ps = E_1\sqrt{R(x+1)}$, where E_1 is the input energy of pendulum, and R is the resilience.

Values of x, E_1, and R for various samples can be determined experimentally, and from them the value of ps, the product of the maximum pressure and indentation, can be plotted against the measured energy loss at the back of the sample. In Figure 3 the values for two widely different types of rubber are plotted and, as postulated, a single function relationship of ps against

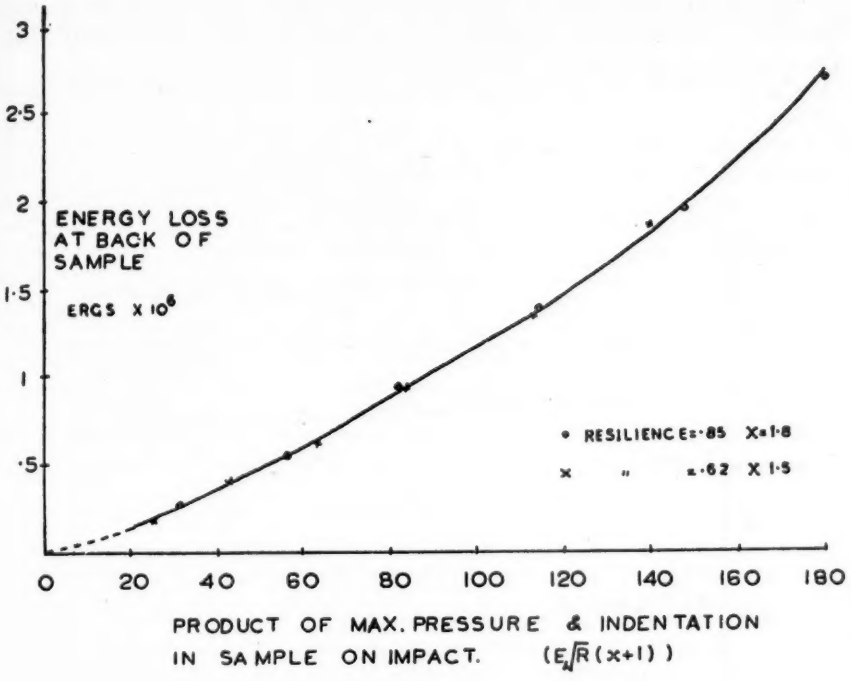

FIG. 3

energy loss exists. This indicates that the cause of the energy loss other than internal friction in the rubber and pendulum air-damping is due to movement of the sample in the holder.

It is recommended that, to obtain comparative resilience results on the various types of pendulums used, corrections should be worked out, which should be added to the observed resilience values to make the results for the various instruments strictly comparable.

The values for the Dunlop pendulum are as follows:

CORRECTIONS TO PENDULUM FOR BLOCK SHUFFLE AND AIR DAMPING
(FOR ANGLE OF FALL 27° 36′ (60 CM. SCALE))

Observed resilience	Shuffle	Air damping	Total
0.30	0.012	0.005	0.017
0.35	0.014	0.005	0.019
0.40	0.015	0.006	0.021
0.45	0.017	0.006	0.023
0.50	0.019	0.006	0.025
0.55	0.021	0.006	0.027
0.60	0.022	0.007	0.029
0.65	0.024	0.007	0.031
0.70	0.026	0.007	0.033
0.75	0.028	0.007	0.035
0.80	0.030	0.007	0.037
0.85	0.031	0.008	0.039
0.90	0.033	0.008	0.041
0.95	0.035	0.008	0.043

The energy losses both at the front and back of the sample are greatly increased if bloom, chalk or rubber dust are present, and it is important that the sample surfaces shall be free from such matter.

Figure 4 shows the observed and the corresponding corrected results for a

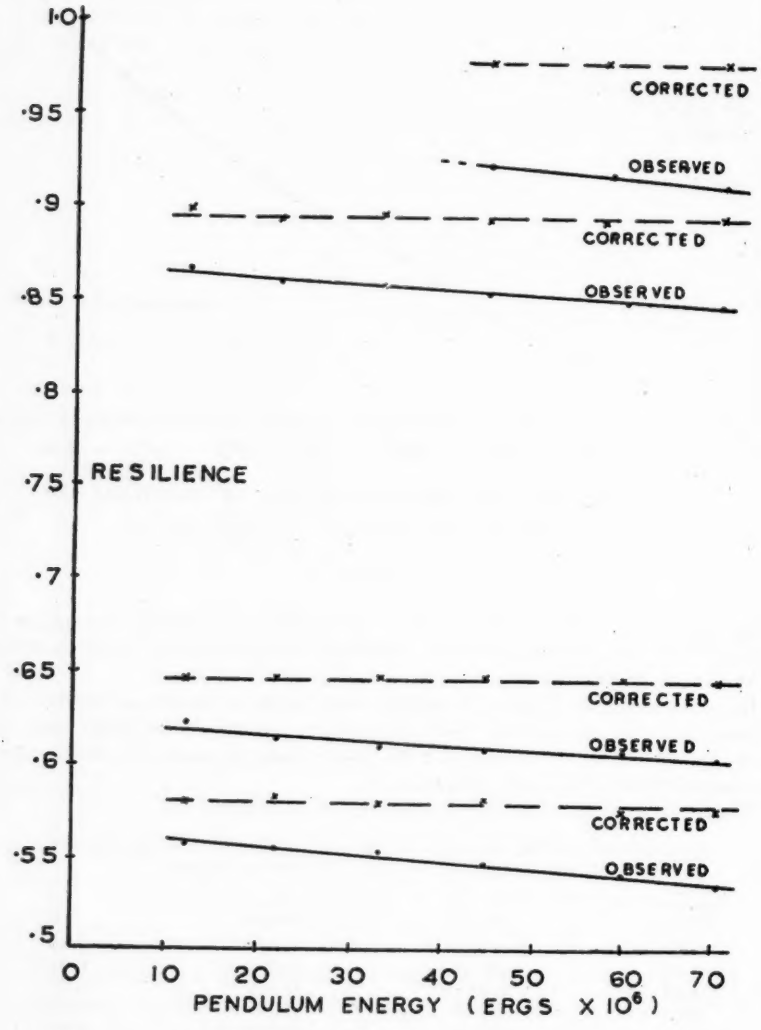

FIG. 4

few widely differing types of compounds, and it will be seen that the resilience is independent of conditions of test if the appropriate correction is applied.

Indentation measurement.—The penetration of the ball into the sample at first sight offers a rapid way of determining the hardness of a rubber, and is used by some workers for this purpose, but if such a determination is to be

comparable with results from the usual penetrometer methods, it must be made at a standard load and not at a standard energy input.

A method of doing this on the pendulum is described in the paper by Jones and Pearce[1] by calculating the maximum pressure set up in the sample at various indentations from the equation: $p = ks^x$, and reading the indentation at a selected value of maximum pressure of 100 kg. If such a calculation is not to be extremely laborious, it is necessary to assume that x has a substantially constant value for all compounds, and it is stated in the paper that the value is 1.55, but an examination of about 100 compounds shows that x varies from 1.2 to 2.0 for different compounds. It is not justifiable, therefore, to calculate the indentations at the standard force by assuming a value of $x = 1.55$, as the actual values of a nominal force value of 100 kg. can vary between 74 kg. and 140 kg., with variation in x from 1.2 to 2.0.

This difficulty can be overcome by calculating the value of x for each compound, but the amount of work is so large that it is scarcely justifiable.

It is more expeditious and accurate to determine the hardness separately by use of one of the standard penetrometer methods[3] (see Hickman, this vol., p. 17), and to confine the use of the pendulum to resilience measurements.

ACKNOWLEDGMENT

In conclusion, I wish to express my thanks to the Directors of the Dunlop Rubber Co. for permission to publish this paper.

REFERENCES

[1] Jones and Pearce, Proc. Rubber Tech. Conf. London 1938, p. 830.
[2] "Rubber Black Testing Procedure", Godfrey L. Cabot, Inc., Oct. 1940; "Columbian Colloidal Carbons", Columbian Carbon Company, 1938.

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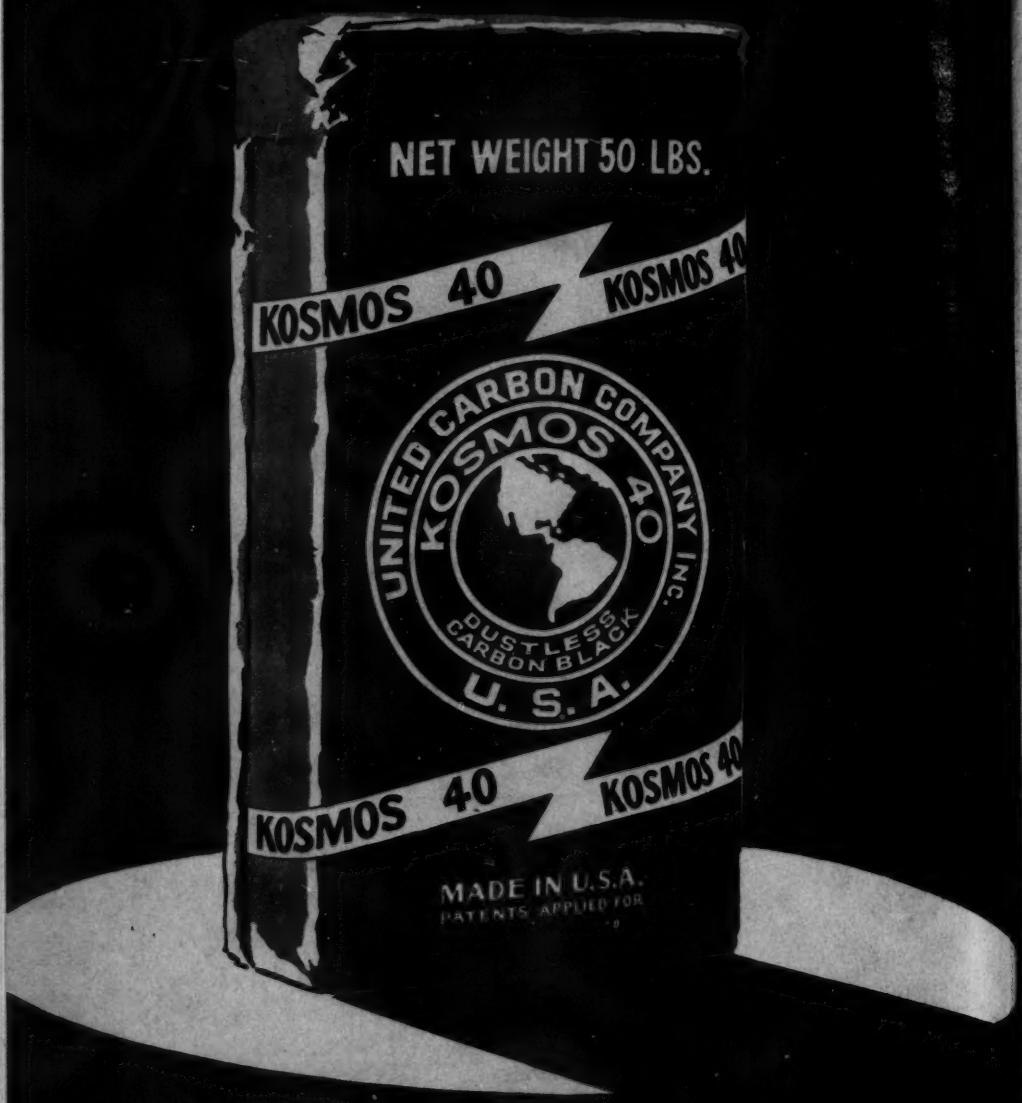

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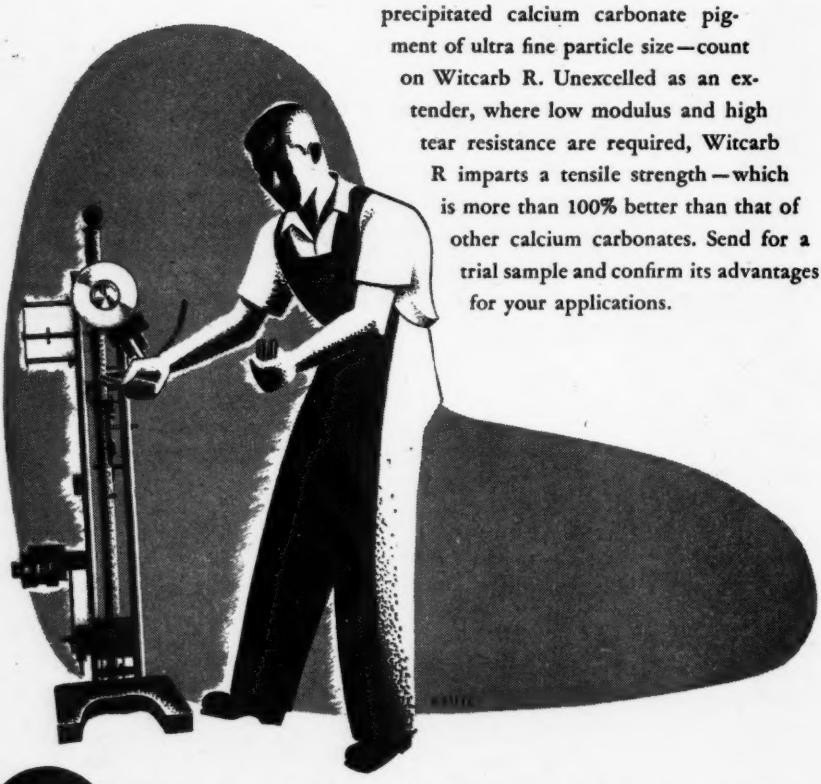

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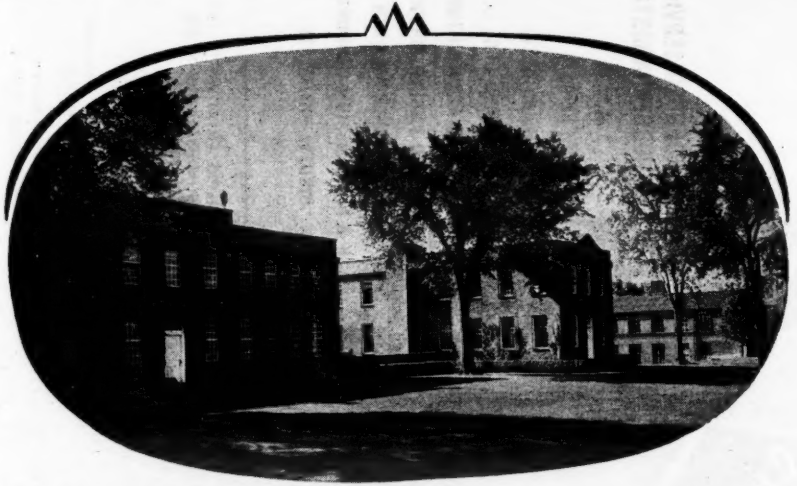

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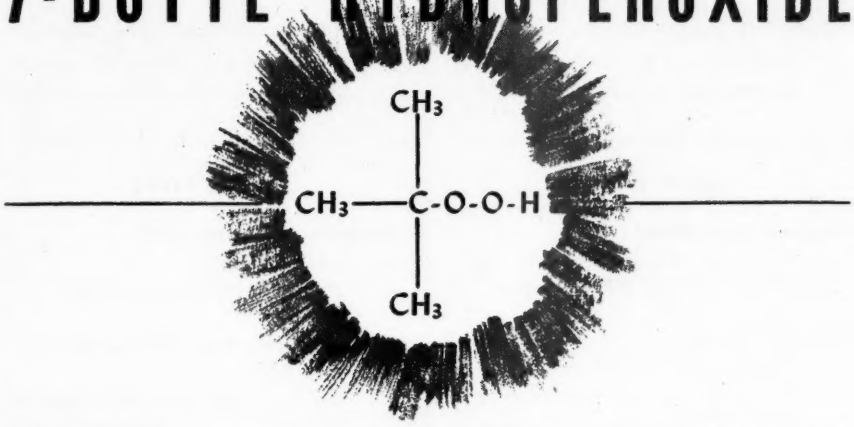

GENERAL DESCRIPTION

t-Butyl Hydroperoxide is a new, organic, alkyl peroxide which offers extremely interesting possibilities. It is standardized at a concentration of 60% (10.66% available oxygen). Use of the proper activators increases the rate of release of the oxygen.

SUGGESTED USES

1. As a catalytic agent in one or two phase polymerizations. (*t*-Butyl Hydroperoxide has proved to be an excellent catalyst for polymerizing Styrene, as well as certain Elastomers such as Buna S.)
2. As a drying accelerator in oils, paints, varnishes, etc.
3. As a combustion accelerator for heavy fuel oils used in Diesel engines.
4. As an accelerator in the curing of synthetic resins.
5. As an accelerator in the vulcanization of certain synthetic rubbers.
6. As an oxidation agent for laboratory purposes.

PROPERTIES

Molecular Weight		90
Specific Gravity @ 25° C.	(60% concentration)	0.859
Boiling Point	"	82–83° C.
Freezing Point	(60% concentration)	−30° C.
Flash Point	"	18.3° C.
Refractive Index @ 25° C.	"	1.3960
Available Oxygen	"	10.66%
Color	"	Water White
pH of 1 part 60% Conc. in 10 parts water		4
Stability		Completely stable up to 76.6° C.
Solubility:	60% concentration in water	11%
	Water in 60% concentration	5%
	In short chain aliphatics	Excellent
	In aromatics	Excellent

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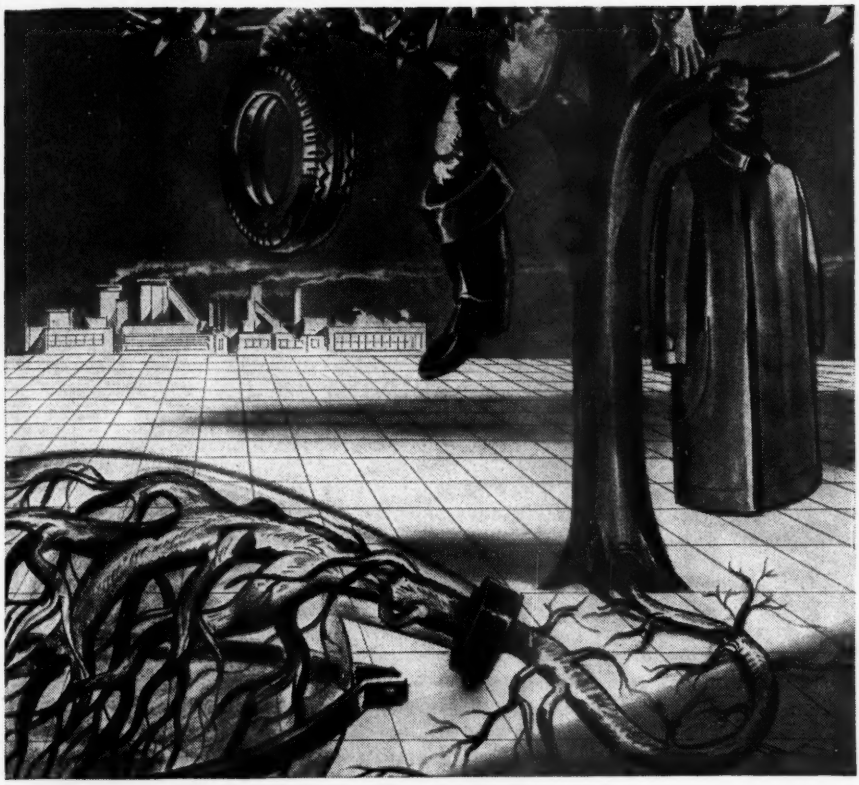

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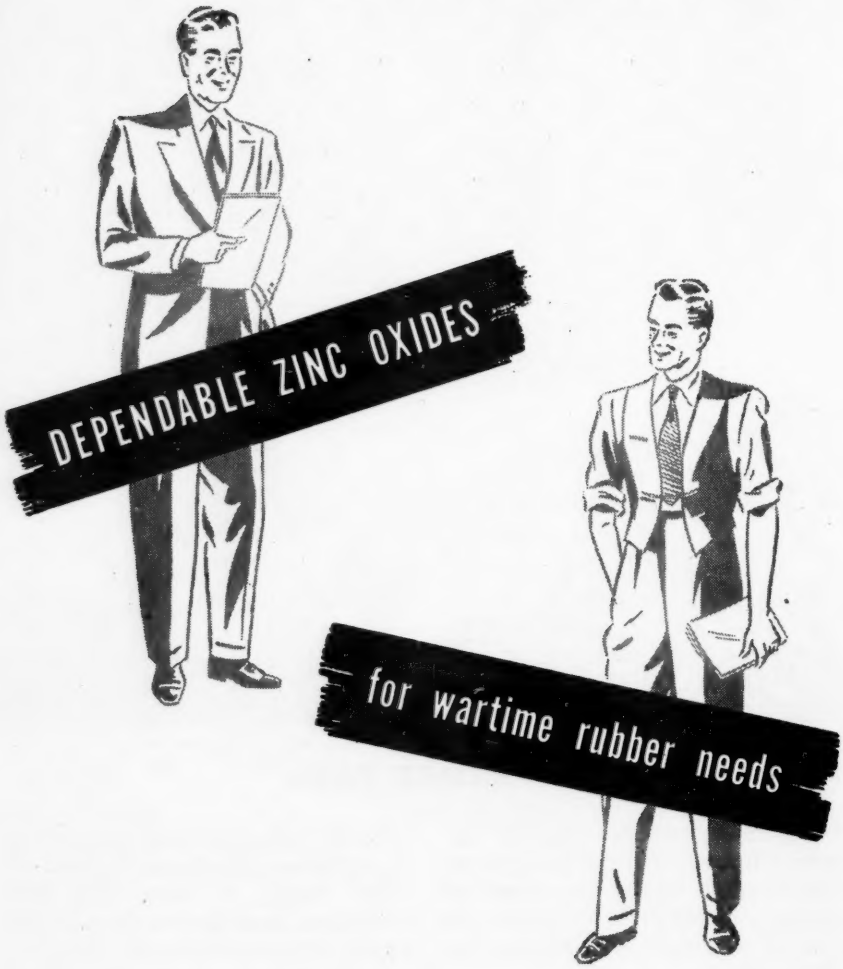

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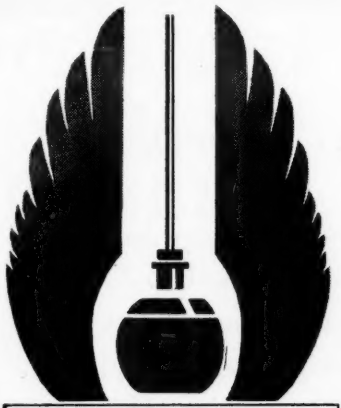

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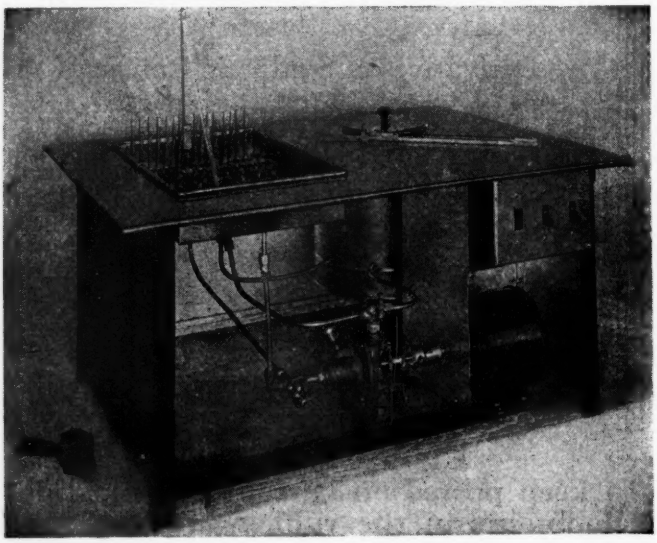

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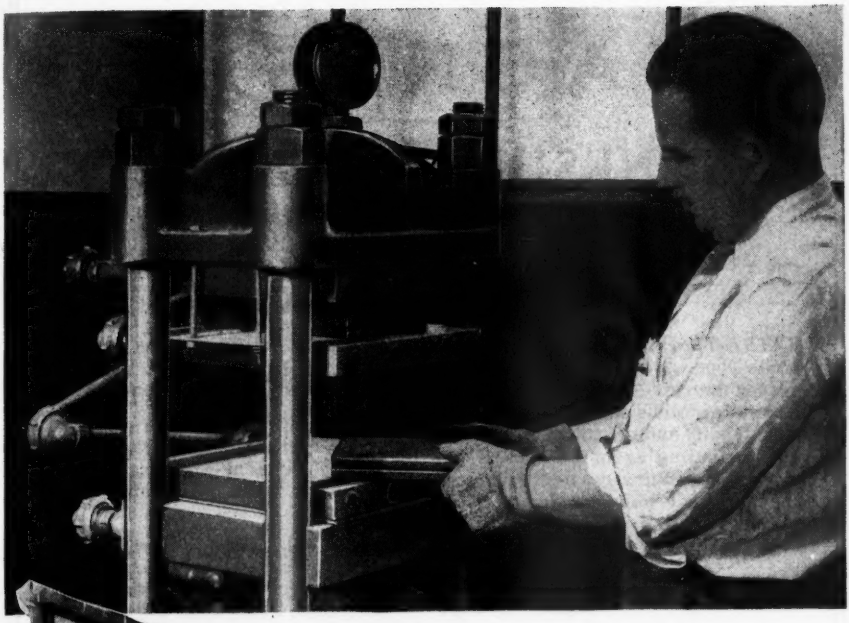

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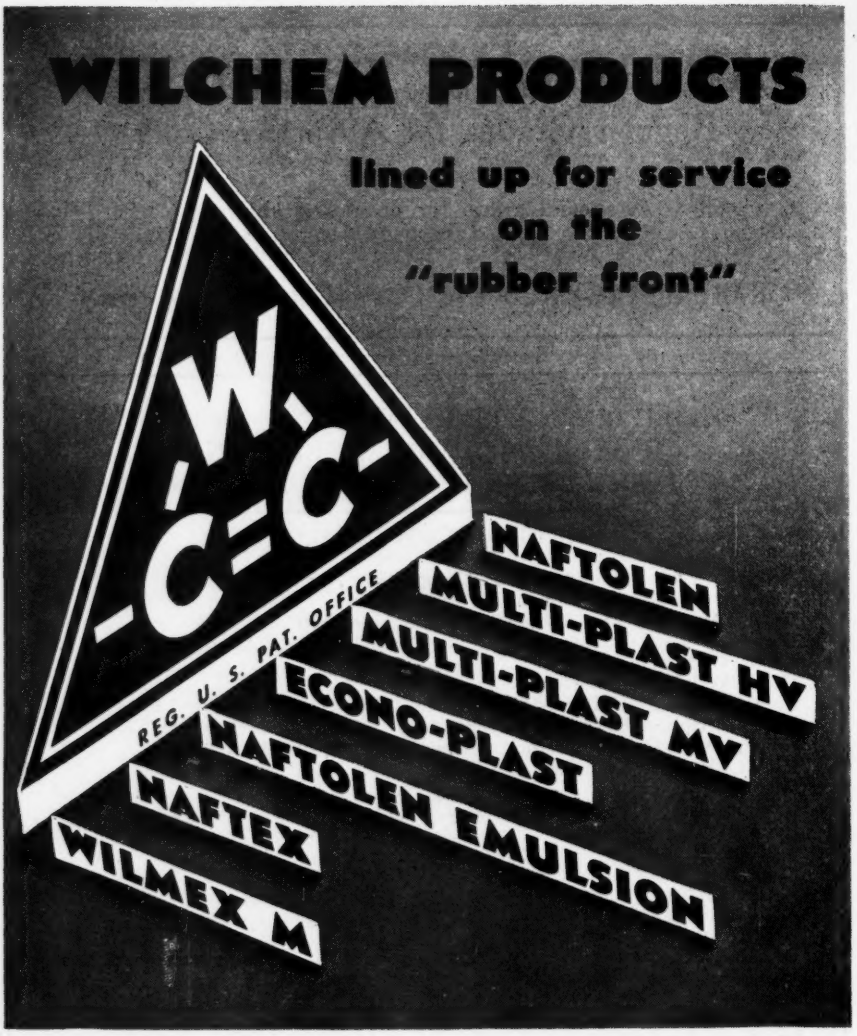

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